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Earth Sciences Division

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Modeling Non-isothermal Multiphase Multi-species Reactive Chemical Transport in Geologic Media

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Abstract

The assessment of mineral deposits, the analysis of hydrothermal convection systems, the performance of radioactive, urban and industrial waste disposal, the study of groundwater pollution, and the understanding of natural groundwater quality patterns all require modeling tools that can consider both the transport of dissolved species as well as their interactions with solid (or other) phases in geologic media and engineered barriers. Here, a general multi-species reactive transport formulation has been developed, which is applicable to homogeneous and/or heterogeneous reactions that can proceed either subject to local equilibrium conditions or kinetic rates under non-isothermal multiphase flow conditions. Two numerical solution methods, the direct substitution approach (DSA) and sequential iteration approach (SIA) for solving the coupled complex subsurface thermo-physical-chemical processes, are described. An efficient sequential iteration approach, which solves transport of solutes and chemical reactions sequentially and iteratively, is proposed for the current reactive chemical transport computer code development. The coupled flow (water, vapor, air and heat) and solute transport equations are also solved sequentially. The existing multiphase flow code TOUGH2 and geochemical code EQ3/6 are used to implement this SIA. The flow chart of the coupled code TOUGH2-EQ3/6, required modifications of the existing codes and additional subroutines needed are presented.

Contents

1. Introduction

The assessment of mineral deposits (e.g. copper deposit), the analysis of hydrothermal convection systems, the performance of radioactive, urban and industrial wastes disposal, the study of groundwater pollution, and an understanding of natural groundwater quality patterns all require modeling tools that consider both the transport of dissolved species as well as their interactions with solid (or other) phases in geologic media and engineered barriers. In the past decade, coupled models accounting for complex hydrological and chemical processes, have been developed [Cederberg et al., 1985; Liu and Narasimhan, 1986; Yeh and Tripathi, 1991; Simunek and Suares, 1993; Steefel and Lasaga, 1994; Walter et al., 1994; White, 1995; Xu, 1996; and Gérard et al.; 1997]. Two major approaches have been used to solve the problem: (1) the direct substitution approach (one-step) which substitutes directly the chemical equations into the transport equation (DSA), and (2) the sequential iteration approach (two-step) which solves the transport and the chemical equation separately in a sequential manner following an iterative procedure (SIA). An important aspect of any reactive solute transport code is its ability to deal with a wide range of chemical processes in complex hydrodynamic systems. Most published and available codes fall into one of three categories: (1) codes with highly sophisticated geochemical subroutines, and a very simplistic representation of hydrodynamic processes; (2) codes which incorporate water flow and solute transport processes in a rigorous manner but account for chemical processes in an oversimplified form; and (3) codes which can handle rigorously both hydrodynamic and hydrogeochemical processes but are suited only for some specific applications. Some of the existing codes are applicable only to one-dimensional steady-state flow regimes, or uniform velocity over the whole domain, or very simple boundary conditions, or simplified transport capabilities such as mixing-cell and explicit backward finite difference methods. Most often, codes consider only isothermal conditions, ignoring temperature effects. Available codes incorporating a multiphase flow model for unsaturated media have very limited chemical reaction capabilities.

There is a clear need for the development of a general purpose and numerically efficient code that can handle all relevant hydrodynamic, thermal and hydrochemical processes. The code

should accommodate all the above mentioned processes for any arbitrary set of chemical species including dissolved species, mineral phases, gas phases, sorbed species and exchanged ions. In addition, it should be able to deal with multiphase flow in both fractured and porous media. General flow and chemical boundary conditions should be also considered. For user convenience, a comprehensive chemical database should be incorporated.

Here, a general multi-species reactive transport formulation has been developed, which is applicable to homogeneous and/or heterogeneous reactions that can proceed either subject to local equilibrium conditions or kinetic rates under non-isothermal multiphase flow conditions. Two numerical solution methods, direct substitution approach (DSA) and sequential iteration approach (SIA) for solving the coupled complex subsurface thermo-physical-chemical processes, are described. An efficient sequential iteration approach, which solves transport of solutes and chemical reactions sequentially and iteratively, is proposed for the current reactive chemical transport computer code development. The coupled flow (water, air and heat) and reactive chemical transport equations are also solved sequentially. The existing multiphase flow code TOUGH2 and geochemical code EQ3/6 are used to implement this SIA. The flow chart of coupling TOUGH2-EQ3/6, possible modifications of the existing codes and additional subroutines needed are presented.

2. Mathematical Formulation

2.1 General reactive chemical transport equations

The purpose of this section is to derive a general multi-species reactive transport formulation which is applicable to homogeneous and/or heterogeneous reactions that can proceed either subject to local equilibrium conditions or kinetic rates under non-isothermal multiphase flow conditions. To achieve this, we first establish stoichiometric relationships among various types of chemical species such as aqueous, gaseous, precipitated, exchanged and sorbed species (details regarding chemical reactions are given in the following section). Then, transport equations for mobile species (aqueous and gaseous) are derived. When aqueous reactions proceed according to local chemical equilibrium, the number of transport equations is reduced.

A chemical system is made up of a set of atomic constituents or elements. A chemical species is defined as any chemical entity distinguishable from the rest due to (1) its elemental composition, or (2) by the phase in which it is present. For instance, gaseous CO_2 is a different species from aqueous CO_2 and aqueous Na^+ is different from exchanged Na^+.

It is assumed that a hydrochemical system contains N_1 aqueous species, and N_R^1 aqueous reactions can take place which can be written as (see Nomenclature at the end of the paper):

$$0 \Leftrightarrow \sum_{j=1}^{N_1} v_{ji}^{1*} S_j^1 \qquad i = 1, ..., N_R^1 \qquad (2.1)$$
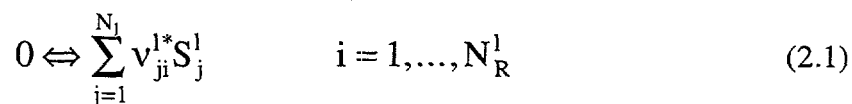
where S_j^1 is the chemical formula of the j-th aqueous species (the superscript 1 stands for the aqueous phase), N_R^1 is the number of aqueous reactions in the aqueous phase, and v_{ji}^{1*} is the stoichiometric coefficient of j-th aqueous species in the i-th reaction. An aqueous species may be

associated only with one gaseous species, such as aqueous CO_2 corresponding to gaseous CO_2 as follow:

$$S_j^g \Leftrightarrow S_j^l \qquad j = 1, ..., N_1 \qquad (2.2)$$

where S_j^g is the chemical formula of the j-th gaseous species. It should be noted that some aqueous species may not have corresponding gaseous species at ambient temperature and pressure such as aqueous Na^+.

N^p minerals may interact with aqueous species by dissolution or precipitation reactions:

$$S_m^p \Leftrightarrow \sum_{j=1}^{N_1} v_{mj}^p S_j^l \qquad m = 1, ..., N^p \qquad (2.3)$$
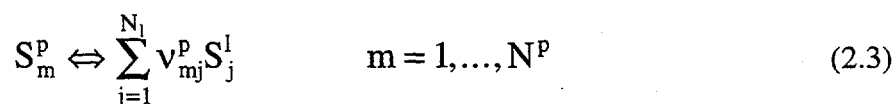
where S_m^p is the chemical formula of the m-th precipitated species (mineral), N^p is the number of minerals that may be present, and v_{mj}^p is the stoichiometric coefficient of j-th aqueous species in the m-th precipitated species. Each aqueous species may have a corresponding exchanged species such as K^+ to $K - X$ ($-X$ represents an ion exchange site):

$$S_j^w \Leftrightarrow S_j^l \qquad j = 1, ..., N_1 \qquad (2.4)$$
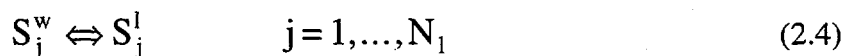
where S_j^w is the chemical formula of the j-th corresponding exchanged species. As seen above for the gas, some aqueous species also may not have corresponding exchanged species. In addition, sorbed species S_i^y can be formed when one or more aqueous species occupy a surface site. Let XOH denote a surface site. A generic surface sorption reaction (adsorption and desorption) can be written as:

$$S_i^y \Leftrightarrow XOH + \sum_{j=1}^{N_1} v_{ji}^y S_j^l \qquad i = 1,2,...,N_y \qquad (2.5)$$
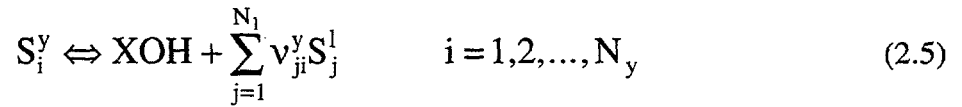
where S_i^y is the chemical formula of the i-th sorbed species, N_y is the number of sorbed species, and v_{ji}^y is the stoichiometric coefficient of j-th aqueous species in the i-th sorption reaction.

All reactions mentioned above may proceed under local chemical equilibrium, may be controlled by various kinetic rate laws (or expressions). Further details regarding chemical equilibrium and kinetic rate laws are given in the next section.

Stoichiometric relationships expressed in (2.1) through (2.5) will be useful for derivation of mass transport equations for reactive mobile (aqueous and gaseous) species. Mass balances for immobile (precipitated, exchanged and sorbed) species are local equations and can be considered as secondary equations. With reference to the standard formulation of multiphase fluid and heat flow [Pruess, 1987 and 1991], the mass transport equations for reactive aqueous species can be written in integral form for an arbitrary flow domain V_n (n labels grid block) as follows:

$$\int_{\Gamma_n} F_l^j \cdot n \, d\Gamma + \int_{V_n} q_l^j \, dv + \int_{V_n} R_l^j \, dv + \int_{V_n} r_g^j \, dv$$
$$= \frac{d}{dt} \int_{V_n} (M_l^j + P^j + W^j + Y^j) \, dv \qquad j = 1,2,...,N_1 \qquad (2.6)$$

where Γ_n is a closed surface around V_n, j labels chemical species (j=one is specified for liquid water), l denotes liquid phase (Note that here the phase index l is written as a subscript, the species index j as a superscript, in accordance with the multi-phase flow model TOUGH2 [Pruess, 1991] convention. However, this is opposite to what it has been done for chemistry,

Equations 2.1-2.5, in which a subscript j labels species index according to customary convection of geochemistry modeling), M_l^j (kg/m^3 medium) is the mass accumulation term of the j-th species in liquid (aqueous) phase, P^j, W^j, Y^j are the mass per unit medium volume (kg/m^3) of the j-th species associated with precipitated, exchanged and sorbed species, respectively. F_l^j (kg/m^{2}s) is mass flux of the j-th aqueous species, q_l^j (kg/m^{3}s) is an external source/sink term of the j-th species in the liquid phase, R_l^j is the internal mass generation rate (kg/m^{3}s) from reactions in the aqueous phase (homogeneous reactions), which is a summed value since species j may be involved in a number of aqueous reactions and r_g^j is the mass generation rate due to gas dissolution ($r_g^j < 0$ for gas exsolution).

The mass transport equations of reactive gaseous species can be similarly written as:

$$\int_{\Gamma_n} \mathbf{F}_g^j \cdot \mathbf{n} \, d\Gamma + \int_{V_n} q_g^j \, dv - \int_{V_n} r_g^j \, dv = \frac{d}{dt} \int_{V_n} M_g^j \, dv \qquad i = 1,2,...,N_1 \qquad (2.7)$$

where symbols have the same meaning as in (2.6) for aqueous species, except that subscript g replaces l for the gas phase.

By adding (2.7) to (2.6) for corresponding aqueous and gaseous species, the gaseous species dissolution rate terms r_g^j disappears and we have:

$$\int_{\Gamma_n} \mathbf{F}^j \cdot \mathbf{n} \, d\Gamma + \int_{V_n} q^j \, dv + \int_{V_n} R_l^j \, dv$$

$$= \frac{d}{dt} \int_{V_n} (M^j + P^j + W^j + Y^j) \, dv \qquad j = 1,2,...,N_1 \qquad (2.8)$$

9

where the symbols without subscripts l or g denote sums over the liquid and gas phases. It should be pointed out that implicit in (2.8) is equilibrium phase partitioning between aqueous and gaseous species.

The mass accumulation terms in the fluid phases are:

$$M^j = \phi S_l \omega^j (c^j + c_g^j) \tag{2.9}$$

where ϕ is porosity, S_l is saturation of liquid phase, ω^j (g/mol) is molecular weight of species j, and c^j (mol/l solution) is the molarity (molar concentration) of aqueous species j, and c_g^j is the concentration of the corresponding gaseous species expressed in terms of moles per one liter of solution. It should be noted that the units in Equations (2.6-2.8) are kg/m³s by using standard geochemical convention of expressing molecular weight in g/mol and concentration in mol/l, accumulation terms are obtained in units of g/l $\equiv$ kg/m³, which is consistent.

The mass of species j associated with mineral phases is:

$$P^j = \omega^j \phi S_l \sum_{m=1}^{N^P} v_{jm}^p p_m \tag{2.10}$$

where p_m is the m-th mineral amount or concentration (moles per liter of solution).

The mass of species j associated with corresponding exchanged species is:

$$W^j = \omega^j \phi S_l w^j \tag{2.11}$$

w^j is the exchanged concentration of the j-th species (in terms of moles per one liter of solution).

The mass of species j associated with sorbed species is:

$$Y^j = \omega^j \phi S_1 \sum_{i=1}^{N_y} v_{ij}^y y_i \qquad (2.12)$$

where y_i is the i-th sorbed species concentration (in terms of moles per one liter of solution).

The mass flux terms can be calculated by using:

$$\mathbf{F}^j = \omega^j \left(\frac{c^j \mathbf{F}_1}{\rho_1} - D_1 \nabla c^j \right) + \omega^j \frac{S_1}{S_g} \left(\frac{c_g^j \mathbf{F}_g}{\rho_g} - D_g \nabla c_g^j \right) \qquad (2.13)$$

where ρ_1 and ρ_g (kg/m³) are densities of the liquid and gas phases, $\mathbf{F}_1$ and $\mathbf{F}_g$ (kg/m²s) are the two phase fluxes, D_1 and D_g (m²/s) are diffusion coefficients in the liquid and gas phases, and S_g is the gas phase saturation. Phase fluxes can be written as a multiphase version of Darcy's law:

$$\mathbf{F}_\beta = -k \frac{k_{r,\beta}}{\mu_\beta} \rho_\beta \left(\nabla P_\beta - \rho_\beta \mathbf{g} \right) \qquad \beta = 1, g \qquad (2.14)$$

where k (m²) is the medium permeability, $k_{r,\beta}$, ρ_β (kg/m³), μ_β (kg/ms) and P_β (Pa) are relative permeability, density, dynamic viscosity and fluid pressure of the β phase, and $\mathbf{g}$ (m/s²) is the gravitational acceleration vector.

In the original version of TOUGH2 [Pruess, 1991], the mass accumulation terms in the fluid phases and mass flux terms are expressed as:

$$M^j = \phi \sum_{\beta=1,g} S_\beta \rho_\beta X_\beta^j \qquad (2.15)$$

and:

$$F^j = \sum_{\beta=1,g} \left(X_\beta^j F_\beta - \rho_\beta D_\beta \nabla X_\beta^j \right) \qquad (2.16)$$

respectively; where X_β^j is mass fraction of species j present in phase β. (2.15) and (2.16) are equivalent to (2.9) and (2.13), respectively. In chemical calculations, it is preferable to use the molal concentration instead of the mass fraction. They are related to each other through:

$$c^{*j} = \frac{1000 \, X_1^j}{\omega^j X_1^w} (\text{mole / kg water}) \qquad (2.17)$$

or

$$c^j = \frac{\rho_1 X_1^j}{\omega^j} (\text{mole / l solution}) \qquad (2.18)$$

where X_1^w is mass fraction of water in the liquid phase. For dilute solutions at ambient temperature, (2.18) is very close to (2.17). In a similar way, the concentration of gaseous species, c_g^j, is related to its mass fraction through:

$$c_g^j = \frac{S_g \rho_g X_g^j}{S_1 \omega^j} (\text{mol / l solution}) \qquad (2.19)$$

Note that the concentration of gaseous species is referred to one liter of solution (liquid).

Similar to chemical species, the energy balance equation can be written as:

$$\int_{\Gamma_n} \mathbf{F}^e \cdot \mathbf{n}\, d\Gamma + \int_{V_n} q^e\, dv = \frac{d}{dt} \int_{V_n} (M^e)\, dv \qquad (2.20)$$

where superscript e represents energy, counterpart of chemical species j. In some cases, reactions such as pyrite oxidation may generate considerable amount of energy according to J. Apps [pers. commom., 1997]. In this case, the energy source terms should include the reaction contributions. The energy accumulation term contains rock and fluid contributions, in units of J per m^3 medium:

$$M^e = (1-\phi)\rho_R C_R T + \phi \sum_{\beta=1,g} S_\beta \rho_\beta u_\beta \qquad (2.21)$$

where ρ_R is rock grain density, C_R is specific heat of the rock grains, T is temperature, and u_β is specific internal energy of phase β. Heat flux contains conductive and convective components:

$$\mathbf{F}^e = -K\nabla T + \sum_{\substack{\beta=1,g \\ j=1,\dots,N_C}} h_\beta^j X_\beta^j \mathbf{F}_\beta \qquad (2.22)$$

where K is the heat conductivity of the rock-fluid mixture, and h_β^j is specific enthalpy of component j in phase β. In general, a dispersive component of heat flux may also be present.

(2.8) and (2.20) constitute the full set of primary governing equations for solving a general non-isothermal multi-species reactive transport problem. They can cope with any type of reactions. However, when aqueous reactions are constrained by local equilibrium, mass transport equations (2.8) are not all independent. The number of governing mass transport equations can then be reduced by directly embedding the equilibrium constraints. The derivation of this will be given in the next paragraph.

13

2.2. Transport equations for a aqueous equilibrium system using an example of pyrite dissolution

Not all species are needed to describe the equilibrium chemical system. We introduce the concept of "components" or "basis species" to denote a reactive chemical system. This subset of species is strictly necessary to fully describe the system. Although the N_E atomic constituents could serve as a set of components, they are never used as such because the constituents themselves are rarely present in aqueous phases. For this reason, it is more convenient to select as components a subset of N_C chemical species, with $N_E = N_C$. These N_C aqueous species are also known as the primary (or basis or master) species. The remaining species are called secondary species, which may include aqueous, gaseous, precipitated, exchanged and sorbed species. The number of secondary species must be equal to the number of reactions taking place, N_R. If the total number of species is denoted by N_T, it follows that: $N_T = N_C + N_R$

Every species is written as the product of a reaction involving only the components, and no component is written as the product of a reaction involving only the other components. In algebraic terms, the components form as a linearly independent set spanning species space. Any of the secondary species is represented as a linear combination of the set of primary species such as:

$$S_i^s = \sum_{j=1}^{N_C} v_{ij} S_j^p \qquad i = 1, \ldots, N_R \qquad (2.23)$$

where S_j^p is the chemical formula of the j-th primary species, S_i^s is the chemical formula of the i-th secondary species, and v_{ji} is the stoichiometric coefficient of j-th primary species in the i-th reaction.

14

This principle can be illustrated by a chemical system relevant for pyrite dissolution. It is assumed that the system is made up of the following species: H^+, H_2O, e^-, SO_4^{2-}, Fe^{2+}, OH^-, HSO_4^-, $FeSO_4(aq)$, HS^-, $H_2S(aq)$, Fe^{3+}, Pyrite (FeS_2). If one selects the first 5 species as the set of components, the rest of secondary species can be written in terms of this set of components:

$$OH^- + H^+ = H_2O \qquad r_1$$

$$HSO_4^- = H^+ + SO_4^{2-} \qquad r_2$$

$$FeSO_4(aq) = SO_4^{2-} + Fe^{2+} \qquad r_3$$

$$HS^- = 9H^+ - 4H_2O + 8e^- + SO_4^{2-} \qquad r_4$$

$$H_2S(aq) = 10H^+ - 4H_2O + 8e^- + SO_4^{2-} \qquad r_5$$

$$Fe^{3+} = Fe^{2+} - e^- \qquad r_6$$

$$pyrite(FeS_2) = 16H^+ - 8H_2O + 14e^- + 2SO_4^{2-} + Fe^{2+} \qquad r_7$$
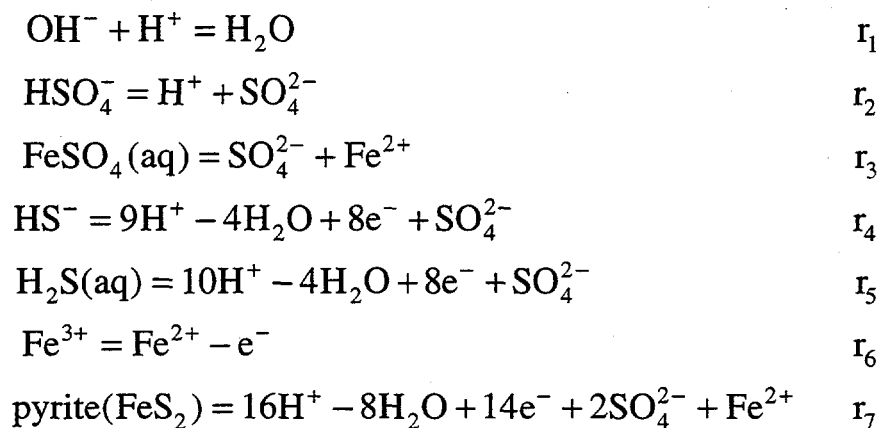
Where r_i (i=1,2,...,7) represent dissociation rates. The reaction stoichiometric matrix is listed in Table 2.

The components can be chosen arbitrarily among all species, but once they have been defined, the representation of the species in terms of this set of components is unique. For the pyrite dissolution system, it is possible to choose HS^- as one of components instead of SO_4^{2-}. The corresponding reaction stoichiometric matrix is given in Table 2.

Table 1. List of species and reaction stoichiometry for the pyrite dissolution system(equilibrium constants are referred from the EQ3/6 database [Wolery, 1992])

	Components					$Log_{10}(K)$
	H^+	H_2O	e^-	SO_4^{2-}	Fe^{2+}	at 25^0C
Species						
H^+	1	0	0	0	0	
H_2O	0	1	0	0	0	
e^-	0	0	1	0	0	
SO_4^{2-}	0	0	0	1	0	
Fe^{2+}	0	0	0	0	1	
OH^-	-1	1	0	0	0	13.995
HSO_4^-	1	0	0	1	0	-2.9791
$FeSO_4(aq)$	0	0	0	1	1	-2.2
HS^-	9	-4	8	1	0	-33.48
$H_2S(aq)$	10	-4	8	1	0	-40.467
Fe^{3+}	0	0	-1	0	1	12.985
$Pyrite(FeS_2)$	16	-8	14	2	1	-83.243

By comparison with Table 1, in Table 2 all stoichiometric coefficients corresponding to sulfide species and their corresponding equilibrium constants are changed.

From the numerical point of view, it is better to select the most abundant species as the primary species; otherwise one may encounter convergence problems especially for redox reactions. In oxidizing conditions, HS^- has extremely low concentrations which pose numerical problems when HS^- is a primary species. In order to obtain a stable numerical treatment, it may be advisable to dynamically "switch" basis species in the course of a simulation (The geochemical package EQ3/6 provides such a basis switching feature). It is particularly relevant

when redox reactions are modeled, because the electron donor (or acceptor) may be present in very low concentrations.

Table 2. *List of species and reaction stoichiometry for the pyrite dissolution system (HS⁻ as the component of sulfide instead of SO_4^{-2} in Table 1)*

	Components					$Log_{10}(K)$
	H^+	H_2O	e^-	HS^-	Fe^{2+}	at 25^0C
Species						
H^+	1	0	0	0	0	
H_2O	0	1	0	0	0	
e^-	0	0	1	0	0	
HS^-	0	0	0	1	0	
Fe^{2+}	0	0	0	0	1	
OH^-	-1	1	0	0	0	13.995
HSO_4^-	-8	4	-8	1	0	31.501
$FeSO_4(aq)$	-9	4	-8	1	1	31.28
SO_4^{2-}	-9	4	-8	1	0	33.48
$H_2S(aq)$	1	0	0	1	0	-6.9877
Fe^{3+}	0	0	-1	0	1	12.985
$Pyrite(FeS_2)$	-2	0	-2	2	1	-16.283

We discuss as an example of extreme concentration changes the redox reaction. from Table 2

$$HSO_4^- = -8H^+ + 4H_2O - 8e^- + HS^- \qquad K = 10^{31.510}$$
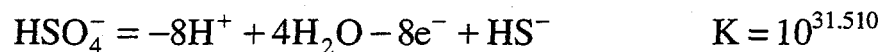
by applying Mass-Action Law,

$$\log_{10}[HS^-] = 31.501 - 8pH - 8pE + \log_{10}[HSO_4^-]$$

where the bracket, [ ], denotes corresponding species activity that is assumed to be close to its concentration. This equation indicates that the concentration of HS⁻ changes by 8 orders of magnitude for every unit change in pH and pE, and that the higher pE values (oxidizing conditions), the lower the HS⁻ concentration. Usually the system of nonlinear chemical reaction equations is solved by Newton-Raphson iteration method. This requires evaluation of derivatives with respect to concentration of the primary species to construct the Jacobian matrix. Extremely low concentrations of the primary species may result in numerical problems such as an ill-conditioned Jacobian matrix.

The total component concentration can be calculated by summing the stoichiometric coefficients multiplied with the corresponding species concentrations in the columns of the stoichiometric matrix. We still use Table 1 as an example. The total dissolved concentration of H^+ and SO_4^{-2} can be calculated as:

$$(H)_T = (H^+)-(OH^-)+(HSO_4^-)+9(HS^-)+10(H_2S(aq))+16(Pyrite)$$

$$(SO_4)_T = (SO_4^{2-})+(HSO_4)+(HS^-)+(H_2S(aq))+(FeSO_4(aq))+2(Pyrite)$$

where the bracket, ( ), denotes concentration of the corresponding species, and ( )$_T$ denotes total dissolved concentration.

In general, letting T_j denote total concentration of component j, one has:

$$T_j = c_j + \sum_{i=1}^{N_R} v_{ij} x_i \qquad (2.24)$$

where c_j is the concentration of the j-th primary species and x_i is the concentration of the i-th secondary species (usually the concentration is denoted by c, to distinguish it from the concentration of the primary species. Here the concentration of the secondary species is denoted by x).

18

The total component concentration T_j is equal to its primary concentration plus all concentrations of its associated secondary species. For total dissolved component concentration C_j, we have:

$$C_j = c_j + \sum_{i=1}^{N_R^l} v_{ij} x_i \qquad (2.25)$$

where summation extends over N_R^l, the number of secondary species in the aqueous phase (equal to the number of aqueous phase reactions).

The primary species (based on the chemical system listed in Table 1) are involved in a number of aqueous reactions. Their concentration changes (or mass generation rates) due to aqueous reactions are:

$$\frac{d[H^+]}{dt} = -r_1 + r_2 + 9r_4 + 10r_5$$

$$\frac{d[H_2O]}{dt} = r_1 - 4r_4 - 4r_5$$

$$\frac{d[e^-]}{dt} = 8r_4 + 8r_5 - r_6$$

$$\frac{d[SO_4^{-2}]}{dt} = r_2 + r_3 + r_4 + r_5$$

$$\frac{d[Fe^{+2}]}{dt} = r_3 + r_6$$

It should be seen that rates of different reactions appear with weighting coefficients from the appropriate columns of the stoichometric matrix (see Table 1). In general, overall generation rates of primary species can be written as:

$$R_j = \sum_{i=1}^{N_R^l} v_{ij} r_i \qquad (2.26)$$

While each secondary species is associated with only one reaction (see Table 1), so that

$$\frac{d[OH^-]}{dt} = -r_1$$

$$\frac{d[HSO_4^-]}{dt} = -r_2$$

$$\frac{d[FeSO_4(aq)]}{dt} = -r_3$$

$$\frac{d[HS^-]}{dt} = -r_4$$

$$\frac{d[H_2S(aq)]}{dt} = -r_5$$

$$\frac{d[Fe^{+3}]}{dt} = -r_6$$

In general, the generation rate of the secondary species is:

$$R_i = -r_i \qquad (2.27)$$

By multiplying (2.27) with v_{ij} and summing over i from 1 to N_R^1, and then adding to (2.26), one has:

$$R_j + \sum_{i=1}^{N_R^1} v_{ij} R_i = 0 \qquad (2.28)$$

The relation expressed in (2.28) is significant for numerically efficient modeling of reactive chemical transport. The same procedure, multiplying by v_{ij} and summing over i, can be applied to mass transport equations (2.8). After this simple mathematical manipulation, internal mass generation terms due to aqueous reactions disappear. The detailed derivation is given in Appendix 1. The resulting mass transport equations are in terms of total dissolved components:

$$\int_{\Gamma_n} \mathbf{F}^j \cdot \mathbf{n} \, d\Gamma + \int_{V_n} q^j \, dv$$

$$= \frac{d}{dt} \int_{V_n} (M^j + P^j + W^j + Y^j) \, dv \qquad j = 1, 2, \ldots, N_c \qquad (2.29)$$

where all terms must be written for total dissolved components rather than species. It should be noted that the derivation of (2.29) is made under the assumption that physical transport parameters such as diffusion and dispersion are not species-dependent. These equations are similar to those of a non-reacting (conservative) species. This is of great relevance for reactive chemical transport modeling because instead of N_1 (total aqueous species) transport equations only N_C (components) equations have to be solved.

Returning to general kinetic reactions, consider the following three reactions:

$$HS^- = 9H^+ - 4H_2O + 8e^- + SO_4^{-2} \qquad\qquad r_4$$

$$H_2S(aq) = 10H^+ - 4H_2O + 8e^- + SO_4^{-2} \qquad\qquad r_5$$

$$H_2S(aq) = H^+ + HS^- \qquad\qquad r_8$$
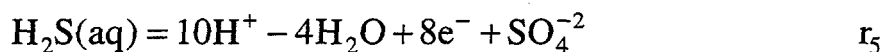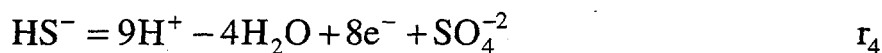
where r_i also denotes equation index. Now $H_2S(aq)$ is associated with two reactions, r_5 and r_8. Its overall generation rate is:

$$\frac{d[H_2S(aq)]}{dt} = -r_5 - r_8$$

If the reactions are at equilibrium, r_8 can be obtained by r_5-r_4. When kinetic rates prevail for aqueous reactions, however, r_8 is an independent reaction. Elimination methods do not apply in this case. All the species involved in kinetic reactions are independent, the mass transport

equations must be written in terms of species [Steefel and MacQuarrie, 1996]. Accordingly for kinetic chemical systems, it is suggested to use the term "multi-species reactive transport", while the term, "multi-component reactive transport" is appropriate for equilibrium systems.

The primary governing equations for non-isothermal multi-species (multi-component in case of equilibrium) reactive transport, which have been given above, need to be complemented with constitutive thermo-physical-chemical relationships, which are local equations and express all secondary variables as functions of a set of primary variables (see Pruess, [1987 and 1991). Here more attention is paid to chemical relationships.

2.3. Chemical reactions

Chemical reactions taking place in subsurface hydrogeochemical systems can be classified as follows:

$$
\text{Reactions} \begin{cases} \text{Homogeneous} \begin{cases} \text{aqueous complexation} \\ \text{Acid - base} \\ \text{Redox} \end{cases} \\ \text{Heterogeneous} \begin{cases} \text{Ion Exchange} \\ \text{Adsorption} \\ \text{Mineral dissolution / precipitation} \\ \text{Gas dissolution / exsolution} \end{cases} \end{cases}
$$
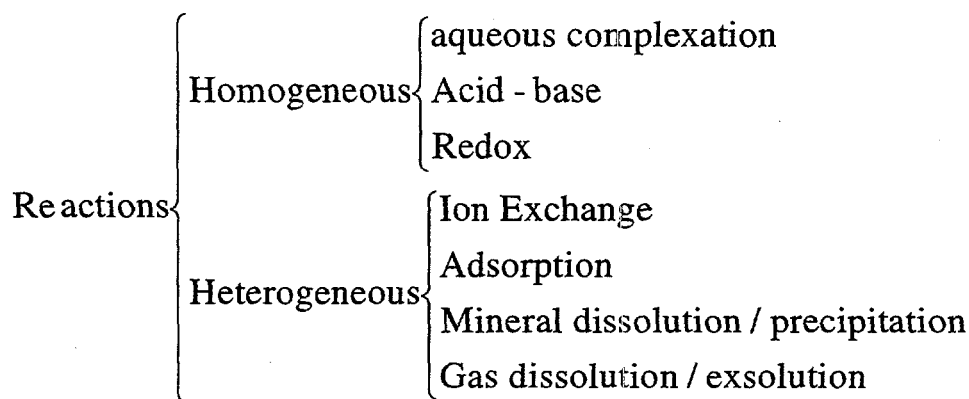
It should be pointed out that although microbial reactions (biological processes) take place in the subsurface environment, they are not considered in this paper.

Although, from a fundamental point of view, reaction progress is governed by kinetics, for practical purposes in water-rock modeling they can be considered as either kinetically or equilibrium-controlled. Two types of chemical equations are required: rate law expressions for kinetics, and mass action equations for equilibrium. The choice between a kinetic and an

22

equilibrium-controlled formulation for a reaction depends on the time and space scale of the system of interest, and above all on the knowledge of the mechanisms and kinetic parameters involved in the reactions.

2.3.1 Homogeneous reactions

<u>Aqueous complexation</u>

In accordance with the thermodynamics of irreversible processes [Prigogine, 1968], if a reaction follows a simple path or a several step path but one of them controls the bulk reaction, its net rate is given by the difference between the forward and backward rate. Consider the dissociation of the i-th aqueous complex (similar to Equation 2.23):

$$S_i^x = \sum_{j=1}^{N_C} v_{ij}^x S_j^p \qquad (2.30)$$

where superscript x denotes an aqueous complex, subscript i denotes the reaction index (or aqueous complex index), and v_{ij}^x is the stoichiometric coefficient of the j-th aqueous primary species in the i-th complex. The forward rate $\left(r_i^x\right)_f$ can be assumed to be proportional to the concentration of species S_i^x :

$$\left(r_i^x\right)_f = \left(k_f^x\right)_i x_i \gamma_i \qquad (2.31)$$

where $\left(k_f^x\right)_i$ is the forward rate constant; and x_i and γ_i denote the concentration and thermodynamic activity coefficient of i-th aqueous complex. Similarly, the backwards rate $\left(r_i^x\right)_b$ is assumed proportional to the product of concentrations of the reactants:

$$\left(r_i^x\right)_b = \left(k_b^x\right)_i \prod_{j=1}^{N_C} c_j^{v_{ij}^x} \gamma_j^{v_{ij}^x} \qquad (2.32)$$

where again $\left(k_b^x\right)_i$ is the backward rate constant; and c_j and γ_j denote the concentration and thermodynamic activity coefficient of j-th aqueous species. The net rate will be:

$$r_i^x = \left(r_i^x\right)_f - \left(r_i^x\right)_b = \left(k_f^x\right)_i x_i \gamma_i - \left(k_b^x\right)_i \prod_{j=1}^{N_C} c_j^{v_{ij}^x} \gamma_j^{v_{ij}^x} \qquad (2.33)$$

The continuous motion of dissolved ions causes numerous collisions making possible the formation of ion pairs and/or dissolved complexes. In most cases these reactions are almost instantaneous, so that they can be effectively considered as equilibrium reactions. At equilibrium, $r_i^x = 0$ so that, from Equation (2.33), one has:

$$K_i = \frac{k_f^x}{k_b^x} = x_i^{-1} \gamma_i^{-1} \prod_{j=1}^{N_C} c_j^{v_{ij}^x} \gamma_j^{v_{ij}^x} \qquad (2.34)$$

where K_i is the equilibrium constant. Thermodynamic activity coefficients γ_i and γ_j can be calculated from the extended Debye-Hückel equation (for low ionic strength solutions) or other equations, including Pitzer's equations when the ionic strength is larger than one. Equation (2.34) allows one to express the concentration of secondary species or aqueous complexes x_i in terms of the primary species concentrations c_j:

$$x_i = K_i^{-1} \gamma_i^{-1} \prod_{j=1}^{N_C} c_j^{v_{ij}^x} \gamma_j^{v_{ij}^x} \qquad (2.35)$$

The dissociation rate of the species x_i can be calculated by:

$$r_i^x = -\frac{dx_i}{dt} \qquad (2.36)$$

Accordingly, the total dissolved concentration of a component, C_j, can be written in an explicit form as a function of the concentration of the N_C primary species according to (2.25) and (2.35).

Treatment of acid-base

These reactions include those involving the transfer of protons H^+. Free proton concentration in the solution can be obtained from the charge balance condition, or alternatively by defining a new variable measuring the proton excess. The first approach is prone to large errors because it requires knowing exactly the chemical composition of the system (i.e., the analytical concentration of all dissolved ions). In addition, in most cases proton concentrations are very small. This means that small errors in the analytical concentration of a dissolved ion may result in a large error in proton concentration. For these reasons, it is usually more convenient to work with the so-called total proton concentration C_H, which is defined as (similar to Equation 2.25):

$$C_H = c_{H^+} + \sum_{i=1}^{N_R^1} v_{iH}^x x_i \qquad (2.37)$$

where c_{H^+} is the concentration of free protons and v_{iH}^x are the stoichiometric coefficients of protons in the acid-base reactions of formation of secondary aqueous species. The total concentration, C_H, represents the net proton balance or "proton excess" of all acid-base reactions taking place in the solution. Contrary to the total concentrations of all other components, C_H may take on negative values. In the previous pyrite dissolution example, we have, from Table 1

25

$$C_H = c_{H^+} - c_{OH^-} + c_{HSO_4^-} + 9c_{HS^-} + 10c_{H_2S(aq)}$$

Notice that acid-base reactions can be analyzed in the same manner as aqueous complexation.

<u>Treatment of redox</u>

The transfer of electrons between two different atoms changes their chemical valence. This transfer is known as an oxidation-reduction (redox) reaction. In spite of taking place in the aqueous phase, these reactions usually do not satisfy the local equilibrium assumption for most real systems [e.g., Ohmoto and Lasaga, 1982; Hostetler, 1984; Lindberg and Runnells, 1984]. This is attributed to the slow rate at which electrons are transferred in some reactions. This transfer requires breaking covalent bonds among light atoms such as S, C, O and H. Some microbes catalyze the redox reactions [see reviews by Ehrlich, 1996; Rittmann and van Briesen, 1996]. According to Liu and Narasimhan [1989], the approaches used by different investigators to model redox reactions in groundwater systems can be summarized as follows: (1) external approach, or hypothetical electron activity approach; (2) oxygen fugacity approach; (3) redox pairs approach; and (4) effective internal approach.

External approach. Contrary to the protons, which exist in reality as dissolved species, the electron concentration is a hypothetical variable. The definition of this virtual concentration is useful because it allows one to complete the redox half-reactions such as (see Table 1)

$$Fe^{+3} = Fe^{+2} - e^-$$
$$H_2S(aq) = 10H^+ - 4H_2O + 8e^- + SO_4^{-2}$$
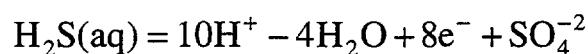
and treat them as the rest of chemical reactions. The overall redox reaction must be the combination of the two half-reactions, such that the species e^- does not appear explicitly, or

$$H_2S(aq) + 8Fe^{+3} + 4H_2O = 10H^+ + SO_4^{-2} + 8Fe^{+2}$$
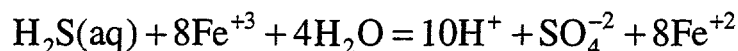
Each redox half-reaction is completed by adding electrons as transferable species. The activity coefficient of this hypothetical species is assumed to be equal to 1. It is possible then to define the total electron concentration C_e as:

$$C_e = c_{e^-} + \sum_{i=1}^{N_R^l} v_{ie}^x x_i \qquad (2.38)$$

where c_e is the "free electron concentration" and v_{ie}^x is the stoichiometric coefficient of the electron in the i-th redox half-reaction.

In the previous pyrite dissolution example (see Table 1), the total electron concentration can be calculated by:

$$C_e = c_{e^-} + 8c_{HS^-} + 8c_{H_2S(aq)} - c_{Fe^{+3}}$$

Similar to acid-base reactions, the total electron concentration C_e represents the net electron balance or "electron excess" for all redox reactions. Thus, C_e may take on positive or negative values. In this way, redox reactions can be treated in the same way as the other reactions. Consideration of redox reactions only requires adding an equation for the electron balance ("operational electrons" according to Yeh and Tripathi, 1989).

Oxygen fugacity approach. Another approach, thermodynamically equivalent to the external approach, is based on attributing the oxidizing potential to the dissolved oxygen. In most natural systems the concentration of dissolved oxygen is well below detection limits [Berner, 1981], and therefore dissolved oxygen also becomes a hypothetical variable. Applying this approach to the previous pyrite dissolution example (see Table 1), we can formulate the reaction system as listed

in Table 3 where primary species e^- (Table 1) is replaced by $O_2(aq)$. By applying the mass action Law to the following reaction:

$$O_2(aq) = 2H_2O - 4H^+ - 4e^- \qquad \log_{10}K = 85.898 \text{ at } 25 \text{ }^\circ C$$

One has

$$a_{O_2(aq)} a_{H^+}^4 a_{e^-}^4 = 10^{-85.898}$$

where water activity is assumed to be 1. Let us consider $O_2(g)$ to be at equilibrium with $O_2(aq)$

$$O_2(g) = O_2(aq) \qquad \log_{10}K = -2.898 \text{ at } 25 \text{ }^\circ C$$
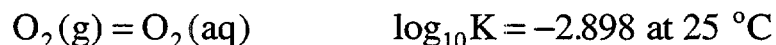
The relationship between oxygen fugacity P_{O_2} (or fractional pressure or partial pressure, a dimensionless quantity and indicating the fraction of total gas pressure that is oxygen pressure) and hypothetical electron activity a_{e^-} can be expressed as:

$$P_{O_2} = \frac{10^{-85.898-2.898}}{a_{H^+}^4 a_{e^-}^4} = 10^{-83+4pH+4pE} \qquad (2.39)$$

where $pE = -\log_{10} a_{e^-}$ and $pH = -\log_{10} a_{H^+}$. Electron activity $a_{e^-} = c_{e^-}$ relates to **Eh** through the Nernst relation:

$$Eh = \frac{2.303RT}{F} pE$$

where F is Faraday's constant (96485 C/mol). At 25 ^{0}C, the relation becomes:

$$Eh = 0.059pE \qquad (2.40)$$

According to a pE-pH diagram given by Sposito [1989]. the range of pE values at a pH of 7 for soil solutions is about, $-6 \leq pE \leq 12$; corresponding to, $10^{-79} \leq P_{O_2} \leq 10^{-7}$. This large range of P_{O_2} values can lead to severe numerical problems in modeling of redox reactions.

Table 3. *List of species and reaction stoichiometry of the pyrite dissolution system using oxygen fugacity approach for redox (equilibrium constant is referred from EQ3/6 database* [Wolery, 1992])

	Components					$Log_{10}(K)$
	H^+	H_2O	$O_2(aq)$	SO_4^{2-}	Fe^{2+}	at 25^0C
Species						
H^+	1	0	0	0	0	
H_2O	0	1	0	0	0	
$O_2(aq)$	0	0	1	0	0	
HS^-	0	0	0	1	0	
Fe^{2+}	0	0	0	0	1	
OH^-	-1	1	0	0	0	13.995
HSO_4^-	1	0	0	1	0	-1.9791
$FeSO_4(aq)$	0	0	0	1	1	-2.2
HS^-	1	0	-2	1	0	138.32
$H_2S(aq)$	2	0	-2	1	0	131.33
Fe^{3+}	1	-0.5	0.25	0	1	-8.4899
Pyrite	2	-1	-3.5	2	1	217.4
$O_2(g)$	0	0	1	0	0	-2.898

Redox pairs approach. The redox potential of a chemical system can be described by means of different redox pairs such as O_2/H_2O, SO_4^{2-}/H_2S, Fe^{3+}/Fe^{2+}, HCO_3^-/CH_4, etc... Usually, the redox potential is governed by the most abundant redox pair. Even though this approach seems to be the most adequate, it is rarely used due to the difficulty of obtaining the analytical concentrations of the two species of a redox pair [Berner, 1981; Wolery, 1992].

Effective internal approach. The effective internal approach originally used in the PHREEQE code, was described by Parkhurst et al. [1980], and later was used by Liu and Narasimhan [1989]. This approach is based on the principle of conservation of electrons, which means that electrons cannot be created or destroyed in chemical reactions although they do not appear in the aqueous phase.

2.3.2 Heterogeneous reactions

Cation exchange.

Cation exchange takes place when free cations in solution exchange with interlayer cations. This process can be described as an equilibrium reaction between an exchangeable cation and an exchange site. A general expression for cation exchange reactions according to the Gaines-Thomas convention is [Appelo and Postma, 1993; Appelo, 1996]:

$$\frac{1}{v_i}S_i + \frac{1}{v_j}\left(X_{v_j} - S_j\right) \Leftrightarrow \frac{1}{v_i}\left(X_{v_i} - S_i\right) + \frac{1}{v_j}S_j \tag{2.41}$$

where v_i and v_j are the stoichiometric coefficients (equal to their charges) of dissolved and interlayer cations, respectively; S_i and S_j denote dissolved cationic species and $\left(X_{v_i} - S_i\right)$

30

and $\left(X_{v_j} - S_j\right)$ represent exchange sites or exchange interlayer cations. For example, **Na-Ca** exchange can be written as:

$$Na^+ + 0.5(Ca - X_2) = 0.5Ca^{+2} + (Na - X)$$
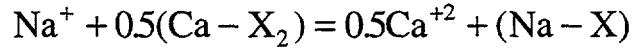
The equilibrium equation for cation exchange is obtained by applying the Mass-action Law to (2.41):

$$K_{ij}^* = \frac{\overline{w}_i^{-1/v_i} \cdot a_j^{1/v_j}}{\overline{w}_j^{-1/v_j} \cdot a_i^{1/v_i}} \qquad (2.42)$$

where K_{ij}^* is the exchange coefficient or selectivity, a_j is the activity of the j-th dissolved species and $\overline{w}_i$ is the activity of the i-th exchanged species. Activities of interlayer cations are approximated by their equivalent fractions of the number of exchange sites [Appelo et al., 1993]. Thus, the activity of the interlayer cation $\overline{w}_i$ is assumed to be equal to its equivalent fraction β_i, and is calculated as:

$$\overline{w}_i \cong \beta_i = \frac{w_i}{\sum\limits_{i=1}^{N_w} w_i} \qquad (2.43)$$

where w_i is the concentration of the i-th interlayer cation and N_w is the total number of such interlayer cations. The sum of concentrations of surface sites or interlayer cations is the so-called cation exchange capacity (CEC). Substituting (2.43) into (2.42) yields the general equation for cation exchange:

$$K_{ij}^* = \frac{\beta_i^{1/\nu_i} \cdot (c_j \gamma_j)^{1/\nu_j}}{\beta_j^{1/\nu_j} \cdot (c_i \gamma_i)^{1/\nu_i}} \tag{2.44}$$

where the activity of each dissolved species a_i has been expressed as the product of its concentration c_i times its activity coefficient γ_i. From this equation, the equivalent fraction of the j-th interlayer cation can be expressed as:

$$\beta_j = \left(K_{ij}^*\right)^{-\nu_j} c_j \gamma_j \left(\frac{\beta_i}{c_i \gamma_i}\right)^{\nu_j/\nu_i} \qquad j = 1, 2, \dots, N_w \tag{2.45}$$

From the definition of equivalent fraction, one has:

$$\sum_{j=1}^{N_w} \beta_j = 1 \tag{2.46}$$

Substituting (2.45) into (2.46) results in:

$$\sum_{j=1}^{N_w} \left(K_{ij}^*\right)^{-\nu_j} c_j \gamma_j \left(\frac{\beta_i}{c_i \gamma_i}\right)^{\nu_j/\nu_i} = 1 \tag{2.47}$$

which for given dissolved concentrations c_j can be solved for the single unknown β_i. This equation is quadratic when cation exchange involves only homovalent and divalent cations. However, when cation exchange involves also trivalent cations a cubic equation is obtained. Once the equivalent fraction β_i is known the rest of the exchange fractions can be calculated from (2.45). The concentration of the j-th exchanged cation w_j (in moles per liter of liquid) can be obtained from the j-th equivalent fraction according to (2.43) through:

$$w_j = \beta_j \, CEC \, \rho_s \, z_j \, \frac{(1-\phi)}{100\phi} \qquad (2.48)$$

where **CEC** is the cation exchange capacity (usually measured as the number of milli equivalents of cations per 100 gram of solid), ϕ is the porosity, ρ_s is the density of the solids (kg of solids per dm³ of solids) and z_j is the cation charge.

Adsorption

Many minerals such as metal oxides, hydroxides and layered silicates exhibit electrically charged surfaces in the presence of natural waters. These surfaces contain ionizable functional groups (eg.: silanol groups in hydrated silica: Si-OH), being responsible for chemical reactions at the surface. The sorption of solutes at the solid surfaces can be described by a set of chemical reactions taking place between aqueous species and specific surface sites (surface complexation). These surface reactions include proton exchange, cation and anion binding via ligand exchange at surface hydroxyl sites (represented here as XOH to avoid confusion with other chemical species). For example, the sorption of a metal can be represented as:

$$XOH + M^{z+} = XOM^{(z-1)+} + H^+$$
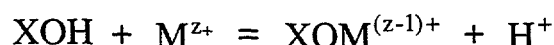
At equilibrium the sorption reactions can be described by the Mass Action Law equation:

$$K_{int\,r} = \frac{\left[XOM^{(z-1)+} \right] a_{H^+}}{[XOH] \, a_{M^{z+}}} \qquad (2.49)$$

where K_{int} is the intrinsic equilibrium constant related to the chemical reaction, usually referred to as the intrinsic constant [Dzombak and Morel, 1990], a is the thermodynamic activity of the aqueous

species and the terms in brackets represent the activity of surface complexes (as moles per Kg of water). To account for the electrostatic field created by the charged surface, the intrinsic equilibrium constant is modified by a surface potential term:

$$K_{ads} = K_{intr} \exp\left(\frac{\Delta z F \psi_0}{RT}\right) \tag{2.50}$$

where R is the gas constant (8.314 J·mol⁻¹·K⁻¹), T the absolute temperature, Δz is the change in the charge of the surface species, F is Faraday's constant (96485 C/mol), ψ_0 is the mean surface potential (V), and K_{ads}, is the apparent equilibrium constant of the overall adsorption process. There are several theoretical models that describe the relationship between surface potential ψ_0 and charge density. These include the triple layer, diffuse layer and constant capacitance models.

In order to represent the sorbed species, an additional set of N_s components (s_k, k = 1, 2, ..., N_s) has to be added to the initial set of N_c aqueous primary species for the previous sorption models. In general, the concentration of a surface complex, y_i, (mol/l solution) can be expressed in terms of the concentration of the two sets of components by means of:

$$y_i = K_i^{-1} \prod_{j=1}^{N_c} c_j^{v_{ij}^y} \gamma_j^{v_{ij}^y} \prod_{k=1}^{N_s} s_k^{v_{ik}^s} \qquad i = 1 \dots N_Y \tag{2.51}$$

where K_i is the equilibrium constant of the desorption reaction as expressed in (2.5), N_Y is the number of surface complexes, v_{ij}^y is the stoichiometric coefficient of the i-th surface complex in the j-th dissolved component, v_{ik}^s is the stoichiometric coefficient of the i-th surface complex in the k-th sorption component. s_k and N_s depend on the surface complexation model selected, for example, in diffuse and constant capacitance models: $N_S = 2$, $s_1 = c_{XOH}$, and $s_2 = \exp(-F\psi_0 / RT)$.

In addition, the conservation of sorption sites must be taken into account:

$$\sum_{i=1}^{N_y} y_i = s_T \qquad (2.52)$$

where s_T is the total concentration of surface sites.

Mineral dissolution/precipitation

The saturation ratio can be expressed as the ratio between the ion activity product (IAP) and the solubility product or thermodynamic equilibrium constant K. For mineral m, one has:

$$\Omega_m = K_m^{-1} \prod_{j=1}^{N_c} c_j^{\nu_{mj}^P} \gamma_j^{\nu_{mj}^P} \qquad (2.53)$$

where m labels mineral index, ν_{mj}^P is the stoichiometric coefficient of j-th aqueous species in the m-th mineral, and K_m is the solubility (or equilibrium) constant of the m-th mineral. For an example of calcite dissolution, $calcite(CaCO_3) = Ca^{+2} + CO_3^{-2}$, we have

$$\Omega_{calcite} = K_{calcite}^{-1} c_{Ca^{+2}} c_{CO_3^{-2}} \gamma_{Ca^{+2}} \gamma_{CO_3^{-2}} \qquad (2.53a)$$

The log Ω_m value is known as the saturation index SI_m. The system reaches the minimum free energy at equilibrium when $\Omega_m = 1$ (or $SI_m = 0$). Saturation ratios Ω_m greater than 1 ($SI_m > 0$) indicate that the m-th mineral will tend to be spontaneously precipitated. On the contrary, when $\Omega_m < 1$ ($SI_m < 0$) the mineral will tend to dissolve spontaneously. The saturation index is proportional to the chemical affinity of the reaction (in Joule mol^{-1}) through:

$$A_m = -RT\ln(\Omega_m) \tag{2.54}$$

Where A_m is chemical affinity of the m-th mineral. The chemical affinity forms the driving force of reaction. The thermodynamic chemical equilibrium condition only states the minimum energy state of the reaction, which is the final state of its evolution, but says nothing about the progress of the reaction or its intermediate steps. Kinetic rate equations offer a way to analyze the chemical evolution (reaction progress) of a reaction and allow the time variable to be incorporated explicitly.

It is well-known that mineral dissolution is a multi-step process. From room to hydrothermal temperatures and under laboratory conditions the mineral dissolution rate is surface-controlled. In accordance with the Transition-State Theory or TST [Eyring, 1935], the rate limiting step of the bulk reaction is the formation of an activated complex at some surface sites of high energy [i.e. Lasaga, 1981; Aagard and Helgeson, 1982; Helgeson et al., 1984]. The surface chemistry is used to propose that the rate limiting step is the formation of a surface complex, precursor of the activated complex. The two complexes are in a state of local equilibrium [e.g. Wieland et al., 1988; Guy and Schott, 1989]. The standard mineral dissolution rate law can be derived from the transition-state theory (TST):

$$r_m = k_d A\, a_{H^+}^n \left(1 - \exp\left(-\frac{A_m}{\sigma RT}\right)\right) A \exp^{-\frac{Ea}{RT}} \tag{2.55}$$

where r_m is the dissolution rate (mol s^{-1}) of the m-th mineral, k_d the dissolution rate constant (mol cm^{-2} s^{-1}), A is the reactive surface area of the mineral, a_{H+} is the inhibitor/catalytic term for pH effects, and n is an experimental exponent, σ is the Temkin number defining the order of the reaction regarding to the chemical affinity ($\sigma = 1$, first order), A is the pre-exponential factor of the Arrhenius rate law (for the temperature dependence), Ea is the apparent activation energy of the reaction (Joule mol^{-1}) which is a function of the solution pH. In derivation of (2.55), it is assumed that protons (H$^+$, H$_2$O, OH$^-$) are the only reacting aqueous species in the formation

reaction and the stoichiometry in framework forming elements of the activated complex and the unaltered silicate is identical [e.g. Helgeson et al., 1984; Murphy and Helgeson, 1987]. The latter tenet implies that one mole of activated complex should be formed, and subsequently detached from the surface, to dissolve one mole of mineral. Therefore, in accordance with the TST, the order of the overall reaction with respect to the chemical affinity is unity.

Within the TST framework, the exponent n is equal to the proton stoichiometry in the formation reaction of the activated complex. The rate constant k_d and the exponent n usually take different values depending on the pH conditions, leading to the well-known U-shaped function. Many experiments have been done to relate the acid from the neutral area to the pH of the point of zero net proton charge, noted pH_{pznpc} [see for example Hochella and Banfield, 1995]. Although consistent results are obtained on for simple oxides, such as SiO_2 [e.g. Brady and Walther, 1992; Dove, 1994], inconsistent ones have been measured on more complex oxides such as alkali-feldspars and kaolinite. Moreover, the temperature dependence of the exponent n measured for kaolinite and albite, for example [see Carroll and Walther, 1990; Hellmann, 1994; Garnor et al., 1995], points out the failure of the standard theory to explain the kinetic dissolution of complex oxides. These discrepancies may be explained by taking into account the inhibitor effect of dissolved aluminum. The formation of an aluminum-deficient or silica-rich surface precursor (2. 56) is the rate-limiting step, which controls the overall dissolution reaction [e.g. Oelkers et al., 1994; Gautier et al., 1994; Schott and Oelkers, 1995].

$$3\,m\,H^+ + M\text{-}O \overset{K^\circ}{\Leftrightarrow} P^\circ + m\,Al^{3+} \tag{2.56}$$
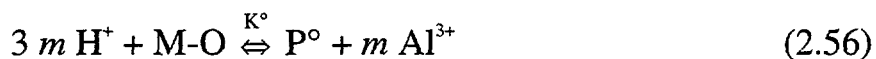
Where M-O represents a potentially reactive surface site (metal-oxygen), m is a stoichiometric coefficient, P° the precursor species and K° the thermodynamic constant of the formation reaction.

A new rate law is derived from the above formation reaction (for details see Oelkers et al., 1994). In its full form the new rate law may be expressed as follows:

$$r_m = k_d A \left\langle \frac{\frac{a_{H^+}^{3m}}{a_{Al^{3+}}^m}}{1 + \frac{K° a_{H^+}^{3m}}{a_{Al^{3+}}^m}} \right\rangle \left(1 - \exp\left(-\frac{A_m}{\sigma RT}\right)\right) A \exp^{-\frac{Ea}{RT}} \qquad (2.57)$$

The authors have measured for albite, K-feldspar and kaolinite a Temkin number (σ) equal to the number of silica mole pers mole of aluminosilicate. The activity term in (2.57) prompts the dependence of the dissolution rate on aluminium speciation close to equilibrium, when the effects of the chemical affinity become sensitive.

The catalytic effects of dissolved alkali (e.g. Na^+, K^+) and earth-alkali (e.g. CA^{2+}, Mg^{2+}) peculiar to silica dissolution can also be predicted with the TST-based rate law proposed in Dove [1994] and introduced in the hydrochemical code KIRMAT [Gérard et al., 1996, 1997]. Other mechanistic equations may be found in the recent literature. Some investigations suggest control by surface defects of the bulk near-to-equilibrium gibbsite dissolution rate [Nagy and Lasaga, 1992; Mogollon et al., 1996].

The standard equation (2. 55) can be used in the code EQ3/6. The order of the bulk reaction with respect to the chemical affinity can be specified as an input parameter, like the species acting in the inhibitor/catalytic term. This approach is still insufficient to compute the above mentioned kinetic equations.

Strictly speaking, mineral precipitation is broken down in the nucleation step and the further crystal growth [e.g. Sunagawa, 1994]. Kinetic precipitation processes are still poorly documented, particularly for the silicate minerals [Steefel and others 1990; Steefel and Van Cappellen, 1990; Nagy and Lasaga, 1993; Nagy, 1995]. This is due to the difficulty in avoiding precursor formation or intermediate compounds, as well as to the slowness of the growth reaction.

Nucleation is a crucial process because it generates the reactive surface area for mineral growth or dissolution. Heterogeneous allophane-halloysite nucleation, Ostwald ripening and transformation to stable kaolinite have been modeled by Steefel and others [1990] or in Steefel and Van Cappellen [1990]. Chang and Yortsos [1994] have tackled silica nucleation-growth during diagenesis. The nucleation process is particularly difficult to model. One should deal at least with the nucleation type (i.e. homogeneous or heterogeneous), the nature of the substrate (heterogeneous nucleation), the nucleation rate, the precursor formation and the nucleus population and size distribution (Ostwald ripening). All these phenomena are dependent on the physical and chemical conditions and the rock composition.

Mineral growth is a multi-step process, as the dissolution, and the slower step controls the growth rate. However, unlike dissolution, it is recognized that several surface processes may successively control the bulk reaction rate according to the chemical affinity and the temperature, which act on the nature of the substrate surface (smooth, rough). To each process is associated a specific kinetic expression [for a review, see Sunagawa, 1994].

The large uncertainties concerning which growth rate law to use and the difficulty to model nucleation processes lead the majority of the geochemical and hydrochemical code developers-users to model precipitation within the tenet of the local equilibrium approximation. The precipitation occurs at equilibrium and the amount formed is given by solving a Mass action law expression. Some codes incorporate a kinetic growth rate, but the parameters to be used (i.e., rate constant) and, above all, its validity has not been checked experimentally.

The geochemical code EQ3/6 includes the reverse standard TST expression though its validity has only been checked over a small oversaturation range for silica [Rimstidt and Barnes, 1980].

Gas dissolution/exsolution

Reactions involving aqueous and gaseous phases are usually assumed to be at equilibrium (this is not always the case, eg. H_2 in air). Similarly, according to the mass action Law, one has:

$$P_i^g \Gamma_i^g K_i^g = \prod_{j=1}^{N_C} c_j^{v_{ij}^g} \gamma_j^{v_{ij}^g} \qquad (2.58)$$

where P_i^g is the fractional pressure (or partial pressure or fugacity) of the i-th gaseous species, Γ_i^g is the activity coefficient, v_{ij}^g is the stoichiometric coefficient of the i-th gaseous species in the j-th primary aqueous species, and K_i^g is the equilibrium constant of the reaction. For low pressures (in the range of atmospheric pressure), the gaseous phase behaves like an ideal mixture. Under these conditions, the activity coefficient Γ_i^g is equal to 1, and the fractional pressure P_i^g is equal to mole fraction and relates to mass fraction through:

$$P_i^g = \frac{\dfrac{X_g^i}{\omega^i}}{\displaystyle\sum_k \dfrac{X_g^k}{\omega^k}} \qquad (2.59)$$

3. Numerical Solution Methods

3.1 Direct substitution approach (DSA)

In this method the chemical reaction source/sink terms are expressed as an algebraic relation between concentrations of the primary species (used as primary variables) and are substituted directly into the mass balance equations. This can be done for kinetic reactions, but in problems involving mineral dissolution or precipitation under the local equilibrium assumption, such a source/sink term is unknown and cannot be substituted into the transport equation. Some authors propose to consider an equilibrium reaction as a particular type of a "very fast kinetically-controlled reaction" [Viswanathan, 1996]. Although equilibrium conditions can be modeled by adopting a kinetic rate with an arbitrarily large rate constant, this approach is prone to severe numerical problems. Here we use a method that can accommodate either kinetics or equilibrium or both by direct substitution approach (DSA). To implement minerals at equilibrium with an aqueous solution in the DSA, N_{equ}^{p} (number of minerals at equilibrium) mass action equations must be added to N_C mass conservation equations (2.29). Aqueous reactions are considered to be at equilibrium and only N_C component transport equations need to be solved. In addition, we also have 1 energy conservation equation (2.20) for each grid block.

The continuum Equations 2.29 of chemical components are discretized in space using the integral finite difference method similar to Pruess [1987 and 1991]. Introducing appropriate volume averages, we have

$$\int_{V_n} (M + P + W + Y)\, dv = V_n (M_n + P_n + W_n + Y_n) \qquad (3.1)$$

where M, P, W and Y are volume-normalized extensive quantities, n labels grid block, and M_n, P_n, W_n and Y_n are average values of them over V_n. Surface integrals are approximated as a discrete sum of averages over surface segments A_{nm}:

$$\int_{\Gamma_n} \mathbf{F} \cdot \mathbf{n} \, d\Gamma = \sum_m A_{nm} F_{nm} \qquad (3.2)$$

where m labels the grid block connected to grid block n, F_{nm} is the average value of the (inward) normal component of $\mathbf{F}$ over the surface segment A_{nm} between volume elements V_n and V_m. The discretization approach used in the integral finite difference method and the definition of the geometric parameters are illustrated in Figure 1.
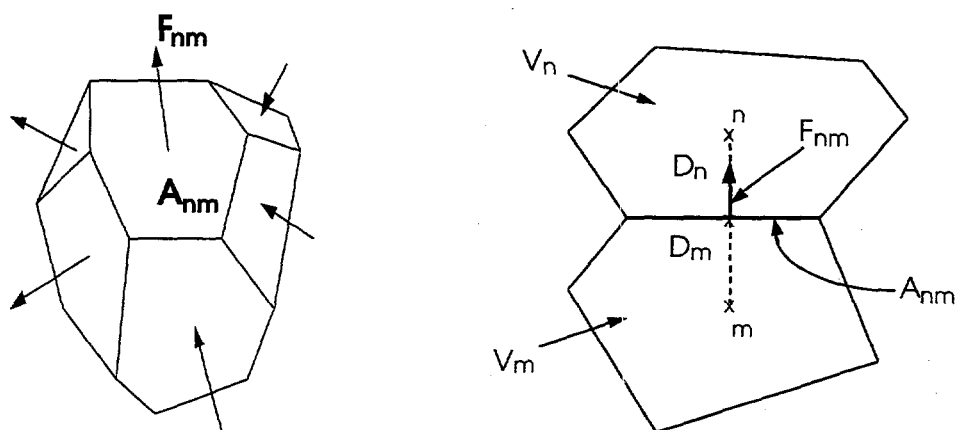
Figure 1. Space discretization and geometry data in the integral finite difference method.

Time is discretized as a first order finite difference. Internal (chemical reaction) source/sink terms are evaluated at the new time level. A general time-weighting parameter θ ($\theta = 1$: fully implicit, $\theta = 0$: explicit) is used for flux and external source/sink terms. Based on the multiphase multicomponent reactive chemical transport equations (2.29) and by separating the mass

42

accumulation in mineral phase into two terms, one due to the kinetic dissolution (or precipitation) and the other due to the equilibrium, we obtain the following set of algebraic equations:

$$\varepsilon_n^{(j)k+1} \equiv \Delta M_n^{(j)k+1} - R_{n,kin}^{(j)k+1} \Delta t + \Delta P_{n,equ}^{(j)k+1} + \Delta W_n^{(j)k+1} + \Delta Y_n^{(j)k+1}$$
$$- \frac{\Delta t}{V_n} \left\{ \sum_m A_{nm} F_{nm}^{(j)k+\theta} + V_n q_n^{(j)k+\theta} \right\} = 0 \qquad j = 1,2,...,N_C \tag{3.3}$$

where k labels the time step, $\Delta t = t^{k+1} - t^k$; $\Delta M^{k+1} = M^{k+1} - M^k$; similarly for $\Delta P_{equ}, \Delta W$ and ΔY. $\Delta P_{n,equ}^{(j)k+1}$ is the change of the mass accumulation due to equilibrium mineral dissolution-precipitation. $R_{kin}^{(j)k+1}$ is the overall kinetic mineral dissolution rate for component j (negative values indicate precipitation), which can be calculated from (similar to Equation 2.10)

$$R_{n,kin}^j = \omega^j \phi_n S_{l,n} \sum_{m=1}^{N_{kin}^P} v_{mj}^P r_m(c_n^1, c_n^2, ..., c_n^{N_C}) \tag{3.4}$$

where m labels the mineral index; r_m is the m-th kinetic mineral dissolution rate (negative values for precipitation), which is an explicit function of concentrations of the primary species as given in (2.55).

Similarly, the energy balance (2.20) can be discretized as

$$\varepsilon_n^{(e)k+1} \equiv \Delta M_n^{(e)k+1} - \frac{\Delta t}{V_n} \left\{ \sum_m A_{nm} F_{nm}^{(e)k+\theta} + V_n q_n^{(e)k+\theta} \right\} = 0 \tag{3.5}$$

The mass transfer due to equilibrium mineral dissolution-precipitation is not specified in the mass action equation. We still use the example of calcite dissolution-precipitation given in (2.53a), $calcite(CaCO_3) = Ca^{2+} + CO_3^{2-}$, at equilibrium, we have

$$K_{calcite} = c_{Ca^{2+}} c_{CO_3^{2-}} \gamma_{Ca^{2+}} \gamma_{CO_3^{2-}}$$

This equation does not include the concentration of the mineral, calcite, since its activity is assumed to be equal to one for the pure phase. Therefore, the amount of dissolved/precipitated mineral cannot be computed explicitly. This is an important feature of this type of reactions that is not shared either by homogeneous reactions or by other heterogeneous reactions. When mineral dissolution or precipitation occurs under equilibrium conditions, N_{equ}^P mass action equations must be added to constrain the equilibrium states for each grid block. According to Equation (2.53), at equilibrium, one has

$$\varepsilon_n^{(m)K+1} \equiv K_m^{-1} \prod_{i=1}^{N_c} c_i^{v_{mi}^P} \gamma_i^{v_{mi}^P} - 1 = 0 \qquad m = 1,2,...,N_{equ}^P \qquad (3.6)$$

where m is equilibrium mineral index, and i is aqueous primary species index. The increments of mass accumulation due to equilibrium mineral dissolution (negative values) or precipitation (positive values) can be written as (according to Equations 2.10)

$$\Delta P_{n,equ}^j = \omega^j \phi S_{l,n} \sum_{i=1}^{N_{equ}^P} v_{ij}^P \Delta p_{n,i} \qquad (3.7)$$

An additional set of primary variables Δp_i $(i+1,2,...,N_{equ}^P)$ must be added to $(N_C + 1)$ variables for each grid block. In addition, ΔW and ΔY can be written in a similar form as (3.7), but they can be directly calculated from concentrations of the primary species according to (2.48) and (2.51).

Equations 3.3 (N_C mass balances), Equation 3.5 (1 energy balance) and Equations 3.6 (N_{equ}^p mass action equations for minerals at equilibrium) provide the set of primary governing equations needed for as many primary unknowns, $(N_C + 1 + N_{equ}^p)$, for each grid block. If a flow domain is discretized into N grid blocks, $(N_C + 1 + N_{equ}^p) \times N$ algebraic equations are needed to describe the entire multiphase multicomponent reactive chemical transport system. These equations are highly non-linear because of non-linear thermophysical parameters and chemical reaction source/sink terms. To handle the non-linearity, we perform Newton-Raphson iteration.

For each grid block, there are $(N_C + 1 + N_{equ}^p)$ primary variables. The primary variables can be chosen as follows: p-pressure (Pa), c_i ($i = 2,3,...,N_C$)-concentrations of the primary species (mol/l solution), T-temperature (^{o}C) and Δp_i ($i = 1,2,...,N_{equ}^p$)-increments of mineral amount (mol/l solution). H_2O is specified with a primary species index of i=1. Its mass balance equation corresponds the primary variable, pressure. Its concentration can be obtained from the other $(N_C - 1)$ concentrations of the primary species.

Denoting this set of primary variables collectively as $(x_i; i = 1,2,...,N_C + 1 + N_{equ}^p)$, the Newton-Raphson iteration process can be written as follows. Demanding that the residuals $\varepsilon_n^{(j)k+1}$ vanish at iteration index $s+1$, and expanding to first order in terms of the residuals at iteration index s, we have

$$\varepsilon_n^{(j)k+1}(x_{i,s+1}) \approx \varepsilon_n^{(j)k+1}(x_{i,s}) + \sum_i \frac{\partial \varepsilon_n^{(j)k+1}}{\partial x_i}\Big|_s (x_{i,s+1} - x_{i,s}) = 0 \qquad (3.8)$$

The system of (3.8) can be written in compact matrix form as

$$J\Delta x = -\varepsilon \tag{3.9}$$

where $\mathbf{J}$ is a square, $\left[(N_C + 1 + N_{equ}^p)N\right]^2$, Jacobian matrix; Δx is an $(N_C + 1 + N_{equ}^p)N$ column vector of increments of primary variables (properly ordered in a sequential manner), and ε is also an $(N_C + 1 + N_{equ}^p)N$ column vector containing residuals. The entries of the Jacobian matrix are

$$J_i^{j,n} = \frac{\partial \varepsilon_n^{(j)k+1}}{\partial x_i} \Big|_s \tag{3.10}$$

which involve derivatives with respect to primary variables. The Jacobian matrix has a banded sparse nature consisting of N^2 square sub-matrices of size $(N_C + 1 + N_{equ}^p)^2$, most of which are zero. The terms involving mass accumulation terms in fluid phases, mineral phases (due to both kinetic and equilibrium dissolution), and exchanged and sorbed phases, only appear in the diagonal sub-matrices. The equations relating to mineral equilibrium constraints (3.6) only appear in diagonal sub-matrices because they are local equations, and are not involved in connections between grid blocks. If there are no minerals at equilibrium, this subset of equations disappears, and the order of the Jacobian matrix reduces to $(N_C + 1)N$.

For each time step, (3.9) are solved iteratively until the residuals are reduced to a small fraction of the total accumulation terms (fluid and solid phases)

$$\max_{n,j} \left| \frac{\varepsilon_{n,s+1}^{(j)k+1}}{(M + P + W + Y)_{n,s+1}^{(j)k+1}} \right| \leq \tau_1 \tag{3.11}$$

When the accumulation terms are smaller than τ_2, $\left|(M + P + W + Y)_{n,s+1}^{(j)k+1}\right| \leq \tau_2$, we impose

an absolute convergence criterion: $\left|\varepsilon_n^{(j)}\right| \leq \tau_1 \cdot \tau_2$.

It should be noted that the conservation equation of water corresponds to the primary variable, pressure. Once concentrations of the primary species are obtained, water mass fraction, activity and all the other chemical variables can be calculated in a straightforward manner.

3.2. Sequential iteration approach

In the sequential iteration approach (SIA), the mass transport equations and chemical reaction equations are considered as two relatively independent subsystems. These are solved separately in a sequential manner following an iterative procedure.

By lumping all mass accumulation terms due to mass transfer between aqueous and solid phases including precipitated (kinetics and equilibrium), exchanged and sorbed species, Equations 3.3 become

$$
\begin{aligned}
\varepsilon_n^{(j)k+1} &\equiv \Delta M_n^{(j)k+1} - R_n^{(j)k+1}\Delta t \\
&- \frac{\Delta t}{V_n}\left\{\sum_m A_{nm}F_{nm}^{(j)k+\theta} + V_n q_n^{(j)k+\theta}\right\} = 0 \qquad j = 1,2,...,N_C
\end{aligned}
\tag{3.12}
$$

where

$$
R_n^{(j)k+1} = R_{n,kin}^{(j)k+1} - \frac{\Delta P_{n,equ}^{(j)k+1}}{\Delta t} - \frac{\Delta W_n^{(j)k+1}}{\Delta t} - \frac{\Delta Y_n^{(j)k+1}}{\Delta t} \qquad j = 1,2,...,N_C
\tag{3.13}
$$

$R_n^{(j)k+1}$ are the overall chemical reaction source/sink terms. To solve mass transport equations, these chemical source/sink terms can be taken equal to the values obtained by solving the

chemical subsystem at the previous iteration. For a multiphase multicomponent flow system, (3.12) are still non-linear even assuming that chemical source/sink terms are known. Fully coupled solution among all components are still required due to non-linear thermophysical relations. This method requires the same memory as the direct substitution approach.

To overcome this drawback, we first only solve simultaneously mass transport equations of water, gas and heat, because these three components are strongly dependent thermophysically. Then all thermophysical parameters, especially fluid velocities, can be obtained. The mass transport equations for other chemical components are linear. Therefore, these equations can be solved in a component by component manner. Then, the resulting total dissolved concentrations are substituted into a chemical sub-model to update chemical source/sinks terms. This process is repeated until satisfying overall convergence criteria, which requires less computing time and memory. Detailed numerical formulation of the proposed approach is presented Appendix 1. This approach is proposed for coupling the multiphase flow code TOUGH2 [Pruess, 1991] and geochemical code EQ3/6 [Wolery, 1992], which is discussed in the following section. It should pointed out that the convergence of the SIA may be slow if there is very strong coupling between chemistry and flow, as for strong dissolution or precipitation reaction with porosity and permeability changes.

The multiphase flow code TOUGH2 [Pruess, 1991] can simulate multiphase multicomponent transport of water, vapor, air and heat in porous as well as in fractured media. EQ3/6 is one of the most comprehensive speciation and reaction path codes available. Using the sequential iteration approach, we can first achieve a coupling of TOUGH2-EQ3/6. Ague and Brimhall [1989] connected EQ3/6 to the transport code TRUST for simulating supergene enrichment of porphyry copper deposits. Their achievement may benefit the current coupling.

On the other hand, we also have reactive transport codes TRANQUI [Xu et al., 1996] and KIRMAT [Gérard et al., 1996, 1997]. TRANQUI considers various types of chemical reactions such as aqueous complexation, acid-base, redox, mineral dissolution, ion exchange and adsorption under equilibrium conditions including a database (modified from EQ3/6 database).

KIRMAT is a 1D thermo-kinetic hydrochemical simulator with several kinetic rate laws, mineral dissolution and dual-porosity capabilities. TOUGH2 offers a fully coupled structure. It is not difficult to directly substitute chemical reaction parts in TRANQUI and KIRMAT to TOUGH2 using the direct substitution approach. We also have access to an enhanced version of TOUGH2 with reactive chemistry [White, 1995]. This code can serve as a reference for verification purposes.

Coupling of TOUGH2 and EQ3/6 by the sequential iteration approach (two-step) is viewed as the most straightforward technique for achieving a comprehensive modeling capability for reactive chemical transport in multiphase flow conditions. A tighter coupling between flow, transport and chemistry can be considered if needed after the sequential approach has been implemented.

4. Coupling TOUGH2-EQ3/6 by Sequential Iteration Approach

This section addresses the general philosophy of how to couple the mass transport code, TOUGH2, with the geochemical speciation and reaction path code, EQ3/6. More attention is paid to the connection and insertion of EQ3/6 into TOUGH2.

4.1. Flow chart

Solute mass transport and chemical reaction equations are solved sequentially following an iterative procedure until convergence (using a sequential iteration approach which is discussed in the previous section 3.2). Flow equations (water, vapor, air and heat) and reactive solute transport equations are also solved sequentially.

After solving the coupled flow equations (water, vapor, air and heat) and computing fluid velocities, solute transport equations can be solved on a component basis (element in EQ6 input) by taking chemical reaction source/sink terms from the previous iteration. Solute transport equations (only in liquid phase) are solved in terms of total dissolved concentrations of the components. In addition, the transport of O_2 (or CO_2) in both liquid and gas phases is considered. The numerical formulation and solution method for solute transport in liquid phase and O_2 transport in the two phases are presented in Appendix 2. The resulting concentrations are substituted into the chemical reaction subroutine EQ6. The temperature distribution obtained from the solution of the coupled flow equations is used to update chemical constants. The solute transport and chemical reaction equations, are iteratively solved until overall convergence. At the end of each global time step physical parameters such as porosity, permeability and reactive surface area are updated. The original TOUGH2 source code can be used with little modification. An additional major subroutine, SOLUTE, is required to solve the solute transport equations. In addition to input and initialization for transport of water, gas and heat, another subroutine, INITCHEM, is required to read and initialize chemical composition and reaction data. A general flow chart for the coupled TOUGH2-EQ3/6 code is shown in Figure 2.

Figure 2. Flow chart of coupled code TOUGH2-EQ3/6 for multiphase flow, solute transport and reactive chemistry


```
┌─────────────────────────────────┐
│ INPUT: Initialize parameters    │
│ for water, vapor, air and heat  │
└─────────────────────────────────┘
              │
              ▼
┌──────────────────────────────────────────┐
│ INITCHEM: Read and initialize chemical    │
│ constants and numerical options, and      │
│ assign chemical state variables to each    │
│ grid block (EQ3)                           │
└──────────────────────────────────────────┘
              │
              ▼
      ⟨ KCYC=KCYC+1 ⟩
      ⟨ Time step: Δt₁ ⟩
```

$KCYC=KCYC+1$

Δt_1

Solve coupled flow equations for water, vapor, air and heat

Temperature distribution

Fluid velocities

COUPLE

SOLUTE: Solve solute transport component by component, and transport of O_2(dissolved + gaseous); time step $\Delta t_2 \leq \Delta t_1$

Total dissolved concentrations

Call **EQ6** on a grid-block-by-grid-block basis (**see following page: Figure 3**)

Convergence

Mass transfer from minerals and

No

Yes

RESET: Update chemical state variables

Update physical parameters

Yes

$\Sigma \Delta t_2 = \Delta t_1$

No

Want more time steps (Δt_1)
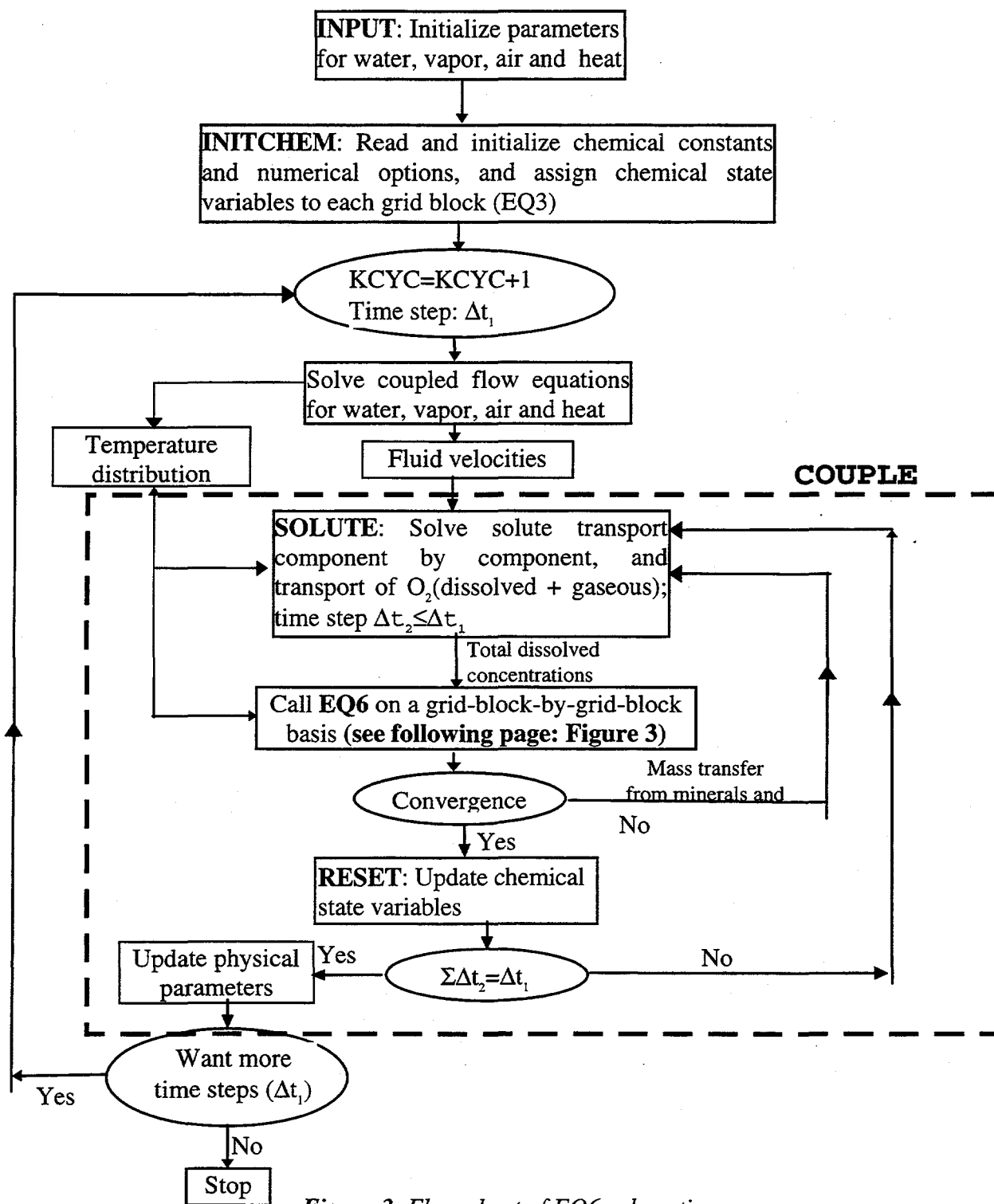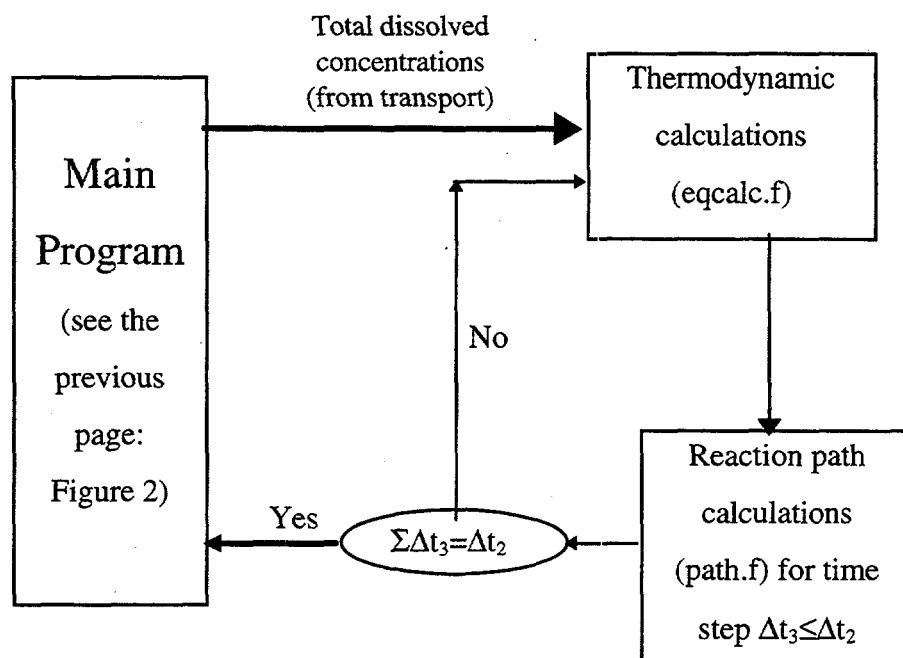
Yes

No

Stop

Figure 3. Flow chart of EQ6 subroutine

51

4.2. Description of additional subroutines

INITCHEM: has the purpose to: (1) read and initialize chemical constants (gas constant ...) and general control data for speciation and reaction path calculations (numerical and printing options) that do not vary with space and time; (2) read initial chemical state variables (such as aqueous and mineral concentrations, kinetic parameters ...) and call EQ3 to assign initial chemical state variables to each grid block; these data may be space-dependent; (3) read chemical concentrations associated with boundary solutions and initialize them using EQ3; they may be space and time dependent.

COUPLE: execute coupling of multi-component solute transport with chemical reaction equations; three subroutines are called: **SOLUTE**, **EQ6**, and **RESET**;

SOLUTE: solves solute transport equations in terms of total dissolved component concentrations on a component (or chemical element: H, O, Al, Si ...) basis and solves O_2 (dissolved and gaseous) transport equations. These equations are linear since the chemical reaction source/sink terms are taken from the previous iteration, which can be solved directly. The resulting total dissolved elemental concentrations are fed into **EQ6**.

EQ6: a subroutine that calls the EQ6 code to perform chemical speciation and reaction path calculations. It is called on a grid-block-by-grid-block basis to update chemical reaction source/sink terms (mass transfer from or to mineral phases). After the solution of the solute transport over Δt_2, the new total dissolved elemental concentrations are transferred into the EQ6 subroutine. The chemical equations are solved by Newton-Raphson iteration technique using concentrations of the basis species as the primary (or master) variables. The initial estimates of the primary variables are taken from the previous iteration.

RESET: reset chemical state variables (aqueous and mineral concentrations) for each grid block for next time step calculations.

4.3. Discussion

(1) **Time step control**: Three time stepping levels will be used. The global time step, Δt_1, is controlled by the solution of flow equations (coupled water, gas and heat). During a time interval of Δt_1, multiple steps Δt_2, or $\sum \Delta t_2 = \Delta t_1$, can be used for solution of solute transport equations. For each grid block, the time step used for solving solute transport may be too large for reaction path calculations (**EQ6** subroutine); its time step Δt_3^n (superscript n labels grid block index) can follow $\sum \Delta t_3^n = \Delta t_2$. Note that reaction path calculations are grid block dependent; each grid block may have its own sub-time discretization pattern, depending on its convergence behavior. For example, a grid block at a redox front may need many very small time increments for a single Δt_2.

53

(2) **Chemical reaction input**. The original input files of EQ3 and EQ6 should be merged and split into two parts (see Appendix 4). The first part consists of general control and option data. The second contains chemical state variables (such as concentrations of aqueous species and minerals, temperature ...) which is grid block, time step (even iteration) dependent, and which have to be internally updated after at initial time they are assigned from INITCHEM.

(3) **Chemical output**. Many EQ6 output statements should be modified or deleted. A new output subroutine for reactive chemical transport, **WRITECHE**, will be set up to write chemical state variables vs. space and time at user specified intervals. In EQ6, the output data are written versus the reaction time and progress, at user specified intervals, into a file called TAB. In both EQ3 and EQ6 the partial equilibrium state of the system (aqueous distribution, affinities, reactions rates ...) along with various information on the numerical calculations are compiled into the OUTPUT file. The **WRITECHE** subroutine should be designed to treat this information as well.

(4) **Keep track of chemical state variables**. The number of aqueous species and minerals involved in the reactions may dynamically change (this is also an advantage of EQ6). This requires significant memory. It may need some programming efforts for multi-dimensional dynamic systems.

5. Conclusions

A general multi-species reactive transport formulation has been developed, which is applicable to homogeneous and/or heterogeneous reactions that can proceed either subject to local equilibrium conditions or kinetic rates under non-isothermal multiphase flow conditions. Two numerical solution methods, the direct substitution approach (DSA) and sequential iteration approach (SIA), for solving the coupled complex subsurface thermo-physical-chemical processes, have been described. An efficient sequential iteration approach, which solves transport of solutes and chemical reactions sequentially and iteratively, has been proposed for the present time. In addition, the coupled flow (water, gas and heat) and solute transport equations are also solved sequentially. The existing multiphase flow code TOUGH2 and geochemical code EQ3/6 are used to implement this SIA. The flow chart of coupled code TOUGH2-EQ3/6, required modifications of the existing codes and additional subroutines needed have been presented.

Appendix 1. Derivation of mass transport equation in terms of total dissolved components

Section 2.2 states that when aqueous reactions are at equilibrium only N_C (components) transport equations are needed to be solved rather than N_1 (total aqueous species). These equations are similar to those of a non-reacting (conservative) species for reactive transport without reactions between fluid and non-fluid phases. For the sake of simplicity, this will be demonstrated for water flow in variably saturated porous media. The principle can be easily applied to a multiphase flow condition.

An equilibrium aqueous system composed of N_1 species which are involved in N_R reactions can be uniquely characterized by the concentrations of N_C ($N_C = N_1 - N_R$) primary species. The concentrations of aqueous primary species c_j satisfy transport partial differential equations such as

$$L(c_j) + r(c_j^* - c_j) + R_j = \theta \frac{\partial c_j}{\partial t} \qquad j = 1, 2, ..., N_c \qquad (A1.1)$$

where $L(\ )$ is the linear transport operator which includes both advective and dispersive transport:

$$L(\ ) = (-q \cdot \nabla + \nabla \cdot \theta D \cdot \nabla)(\ )$$

θ is volumetric water content, q is Darcy's velocity, D is dispersion tensor, r is fluid source/sink term (such as injection/pumping), c_j^* is concentration of primary species j associated with source/sink term r, and R_j is the chemical source/sink term of the j-th primary species with

formula S_j. R_j represents the moles of S_j that are created or lost per unit time and unit aquifer volume due to all aqueous chemical reactions in which S_j is involved.

Any secondary aqueous species with formula S_i^x can be written in terms of primary species:

$$S_i^x \Leftrightarrow \sum_{j=1}^{N_C} v_{ij}^x S_j \qquad (A1.2)$$

This reflects that S_i^x is formed entirely from a combination of primary species, v_{ij}^x being the stoichiometric coefficients of such combination. Let r_i^x be the rate of progress of reaction (A1.2), which is positive when proceeding towards the right (decomposition of S_i^x). Therefore, the rate of dissociation of S_i^x is given by

$$r_i^x = -\frac{\partial(\theta x_i)}{\partial t} = \frac{1}{v_{ij}^x}\frac{\partial(\theta c_j)}{\partial t}\bigg|_{x_i} \qquad i = 1, 2, ..., N_X \qquad (A1.3)$$

This equation reflects that one mole of S_i^x dissociates into v_{ij}^x moles of species S_j. In other words, the rate of accumulation of primary species S_j due to this reaction is v_{ij}^x times the dissociation rate of S_i^x.

Inasmuch as primary species can be formed from the dissociation of several secondary species, one has to specify in (A1.3) that the time rate of change of the mass of S_j (per unit aquifer volume), θc_j is caused by the i-th dissociation reaction. The total rate of mass generation for the j-th primary species is

$$R_j = \sum_{i=1}^{N_x} \frac{\partial(\theta c_j)}{\partial t}\bigg|_{x_i} \tag{A1.4}$$

Taking into account (A1.3), this rate R_j is given by

$$R_j = \sum_{i=1}^{N_x} v_{ij}^x r_i^x \tag{A1.5}$$

Secondary species are also mobile and therefore their concentrations x_i satisfy a transport equation similar to (A1.1)

$$L(x_i) + r(x_i^* - x_i) - r_i^x = \theta \frac{\partial x_i}{\partial t} \tag{A1.6}$$

It should be pointed out that the i-th secondary species S_i^x only participates in its dissociation reaction and therefore its chemical sink/source term reduces to $-r_i^x$.

Each secondary species satisfies a transport equation similar to (A1.6). Multiplying each one of them by v_{ij}^x and summing over all N_x secondary aqueous species, one has:

$$L\left(\sum_{i=1}^{N_x} v_{ij}^x x_i\right) + r\left(\sum_{i=1}^{N_x} v_{ij}^x x_i^* - \sum_{i}^{N_x} v_{ij}^x x_i\right) - \sum_{i=1}^{N_x} v_{ij}^x r_i^x = \theta \frac{\partial}{\partial t}\left(\sum_{i=1}^{N_x} v_{ij}^x x_i\right) \tag{A1.7}$$

In arriving at (A1.7), species-independent of the transport operator $L(\ )$ is assumed. The total concentration of the j-th primary species originated in aqueous dissociation reactions as

$$X_j = \sum_{i}^{N_x} v_{ij}^x x_i \qquad\qquad (A1.8)$$

from (A1.5) and (A1.7), it follows that

$$L(X_j) + r(X_j^* - X_j) - R_j^x = \theta \frac{\partial X_j}{\partial t} \qquad j = 1, 2, ..., N_c \qquad (A1.9)$$

This equation shows that X_j satisfies a transport equation identical to that of c_j (Equation A1.1) except for the sign of the sink/source term. In fact, by adding (A1.1) and (A1.9) the source terms cancels out so that

$$L(c_j + X_j) + r\left[(c_j^* + X_j^*) - (c_j + X_j)\right] = \theta \frac{\partial(c_j + X_j)}{\partial t} \qquad (A1.10)$$

Defining the total dissolved concentration of the j-th aqueous primary species, C_j, as $C_j = c_j + X_j$, one can see that in terms of C_j the transport equation is identical in form to that of a conservative species. In fact, from (A1.10) it follows that

$$L(C_j) + r(C_j^* - C_j) = \theta \frac{\partial C_j}{\partial t} \qquad (A1.11)$$

where

$$C_j = c_j + X_j = c_j + \sum_{i} v_{ij}^x x_i \qquad (A1.12)$$

To illustrate this result let us consider an example with the following calcium bearing species: free calcium Ca^{2+}, calcium bicarbonate $CaHCO_3^+$ and dissolved calcium sulfate $(CaSO_4)_{aq}$. In this case, the total dissolved calcium concentration C_{Ca} is given by

59

$$C_{Ca} = c_{Ca} + x_{CaHCO_3} + x_{CaSO_4}$$

where free calcium is assumed to be the primary calcium species. In the absence of heterogeneous reactions involving calcium, the total dissolved calcium behaves like a conservative species.

Appendix 2. Solution of solute transport equations

Most chemical species are only subject to transport in the liquid phase. A few species can be transported in both liquid and gas phases such as O_2 and CO_2. We first derive the numerical formulation of reactive transport in the liquid phase. This will then be extended to transport in both phases for some species.

A2.1. Transport in liquid phase

If reactions taking place in liquid are assumed to be at local equilibrium, mass transport equations can be written in terms of total dissolved component concentrations (see Section 2.2). On the basis of (3.12), and replacing the mass flux $F_{nm}^{(j)}$ by product of the volumetric flux and the dissolved component concentration, numerical formulation of solute transport in the liquid phase can still written as

$$\frac{\Delta t}{V_n} \sum_m A_{nm} u_{nm}^{k+1} C_{nm}^{(j),k+1,s+1/2} =$$

$$\Delta M_n^{(j),k+1} - q_n^{(j)k+1} \Delta t - R_n^{(j),k+1,s} \Delta t \qquad j = 1,2,...,N_C \qquad (A2.1)$$

where u_{nm} is the liquid volumetric flux or Darcy's velocity (m/s), n labels the grid block, j labels the chemical component, l labels liquid phase, k labels the number of the time step, s labels the number of the transport-chemistry iteration (details is given later). For simplicity, in (A2.1) the liquid phase index l is neglected.

The concentration in the flux term of (A2.1) can be evaluated by upstream-weighting or

61

$$C_{nm}^{(j),k+1,s+1/2} = \theta \left[\varepsilon_{nm} C_n^{(j),k+1,s+1/2} + (1 - \varepsilon_{nm}) C_m^{(j),k+1,s+1/2} \right]$$
$$(1-\theta) \left[\varepsilon_{nm} C_n^{(j),k} + (1 - \varepsilon_{nm}) C_m^{(j),k} \right] \tag{A2.2}$$

where

$$\varepsilon_{nm} = \begin{cases} 0 & \text{if} \quad u_{nm} \geq 0 \quad \text{inflow} \\ 1 & \quad u_{nm} < 0 \quad \text{outflow} \end{cases}$$

The mass accumulation terms can be evaluated as

$$\Delta M_n^{(j),k+1} = S_{1,n}^{k+1} \phi_n^{k+1} C_n^{(j),k+1,s+1/2} - S_{1,n}^k \phi_n^k C_n^{(j),k} \tag{A2.3}$$

By substituting (A2.2) and (A2.3) into (A2.1), and then rearranging them in terms of unknowns, $C^{(j),k+1,s+1/2}$ (total dissolved component concentrations), one has

$$\left[S_{1,n}^{k+1} \phi_n^{k+1} - \frac{\theta \Delta t}{V_n} \sum_m A_{nm} u_{nm}^{k+1} \varepsilon_{nm} \right] C_n^{(j),k+1,s+1/2} + \frac{\theta \Delta t}{V_n} \sum_m A_{nm} u_{nm}^{k+1} (\varepsilon_{nm} - 1) C_m^{(j),k+1,s+1/2} =$$

$$\frac{(1-\theta)\Delta t}{V_n} \sum_m A_{nm} u_{nm}^{k+1} \varepsilon_{nm} C_n^{(j),k} - \frac{(1-\theta)\Delta t}{V_n} \sum_m A_{nm} u_{nm}^{k+1} (\varepsilon_{nm} - 1) C_m^{(j),k}$$

$$S_{1,n}^k \phi_n^k C_n^{(j),k} + q_n^{(j)k+1} \Delta t + R_n^{(j),k+1,s} \Delta t \qquad\qquad j = 1,2,...,N_C \tag{A2.4}$$

For the sequential iteration approach, the iteration index s is essential. A new transport-chemistry iteration consists of two parts, transport part denoted by, s+1/2, (it should be noted that ½ does not mean $\Delta t/2$), and chemistry part denoted by, s+1. Equation (A2.4) for each chemical component j is linear if $R^{(j),s}$ is known, and has the same structure as the non-reacting

(conservative) solute transport equation. The chemical reaction source/sink term $R^{(j),s}$ represents mass transfer of component j between aqueous and solid phases. The values of these source/sink terms at the new transport iteration, s+1/2, are evaluated at the previous chemistry iteration, s. The resulting new values of $C^{(j),s+\frac{1}{2}}$, obtained by solving transport equations (A2.1), are substituted into chemical reaction subroutines and one can compute new values of $R^{(j),s+1}$. Transport and chemical reaction equations are iteratively solved until prescribed convergence criteria are satisfied. The essence of this sequential iteration approach is therefore the sequential solution of two independent sets of equations: the transport equations and the chemical equations. The transport equations are solved on a component by component basis, whereas the chemical equations are solved on a grid block basis. These two sets of equations are coupled by updating chemical source/sink terms.

For kinetic mineral dissolution-precipitation, the terms $R^{(j)}$ can be calculated directly from kinetic expressions. For equilibrium, these terms can be obtained indirectly from component mass balance equations. The solution of chemical equilibrium system and calculation of the source/sink terms $R^{(j)}$ are presented in Appendix 3. From the chemistry point of view, equilibrium mineral dissolution-precipitation does not appear an explicit rate expression. To avoid confusion, we write the last term in (A2.4) as

$$R_n^{(j),k+1,s}\Delta t = -\Delta P_n^{(j),k+1,s} \tag{A2.5}$$

where $\Delta P_n^{(j),k+1,s}$ mean mass transfer of component j from the aqueous phase to the mineral phase at iteration n, grid block n and time step k+1 (or called mass accumulation in mineral phases; negative values indicate mass transfer from the mineral phase to the aqueous phase)

Returning to (A2.4), the diagonal term of n-th linear algebraic equation is

$$S_{1,n}^{k+1}\phi_n^{k+1} - \frac{\Delta t}{V_n}\sum_m A_{nm}F_{nm}^{k+1}\varepsilon_{nm}$$

The off diagonal terms are

$$\frac{\Delta t}{V_n} A_{nm} F_{nm}^{k+1} (\varepsilon_{nm} - 1) \qquad m = 1, 2, \ldots, \text{number of connections to } n$$

The right-hand side terms are

$$S_{l,n}^k \phi_n^k C_n^{(j),k} + q_n^{(j)k+1} \Delta t + R_n^{(j),k+1,s} \Delta t \qquad j = 1, 2, \ldots, N_C$$

It can be seen that the coefficient matrix is the same for all chemical components. The matrix depends on space and time discretization, and flow conditions. The equations for different components only differ in right-hand side terms. This means that once the matrix has been factorized by LU decomposition, the solution of the system of equations only requires a backward and a forward substitution, which results in a saving of computing time.

A2.2. Transport in both liquid and gas phases

It is assumed that an aqueous species and its corresponding gaseous species are at local equilibrium such as

$$O_2(g) = O_2(aq)$$
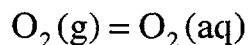
Under this assumption, their concentrations can be calculated as:

$$C = K_g P^g \qquad\qquad \text{(A2.6a)}$$

$$C^g = \frac{10^2}{RT} P^g \qquad\qquad \text{(A2.6b)}$$

where C and C^g are aqueous and gaseous species concentrations (in mol/l), K_g is the equilibrium constant, P^g is the gaseous species partial pressure (in bar), R is the gas constant (8.314 J.mol^{-1}.K^{-1}) and T is the absolute temperature. (index g denotes gas phase, and for liquid phase there is no counterpart l; the same notation for the following equation).

By following the same principle used for transport in liquid phase and by considering (A2.6a) and (A2.6b), Numerical formulation of reactive transport in both liquid and gas phases can be expressed as

$$\left[\left(K_g S_{l,n}^{k+1}\phi_n^{k+1} + \frac{10^2}{RT}S_{g,n}^{k+1}\phi_n^{k+1}\right) - \frac{\Delta t}{V_n}\sum_m A_{nm}\left(K_g u_{nm}^{k+1}\varepsilon_{nm} + \frac{10^2}{RT}u_{nm}^{g,k+1}\varepsilon_{nm}^g\right)\right]P_n^{g,(j),k+1,s+1/2} +$$

$$\frac{\Delta t}{V_n}\sum_m A_{nm}\left[K_g u_{nm}^{k+1}(\varepsilon_{nm}-1) + \frac{10^2}{RT}u_{nm}^{g,k+1}(\varepsilon_{nm}^g-1)\right]P_m^{g,(j),k+1,s+1/2} =$$

$$\left(K_g S_{l,n}^k\phi_n^k + \frac{10^2}{RT}S_{g,n}^k\phi_n^k\right)P_n^{g,(j),k} + q_n^{(j)k+1}\Delta t + R_n^{(j),k+1,s}\Delta t \qquad j=1,2,...,N_g$$

(A2.7)

where N_g is number of gaseous species (in most cases, only a few species can be present in the gas phase such as O_2 and CO_2 that are significant for reactive chemistry). (A2.7) are derived on the basis of the relationship (A2.6) which is specific to dissolved and gaseous species, so we can no longer deal with total component concentration variables, instead species concentration (either gaseous or dissolved species). The structure of equations (A2.7) is the same as that of (A2.4) for transport only in liquid phase . The same solution method can be applied for solving (A2.7). The differences are: (1) coefficients contain contributions from both liquid and gas phases, and (2) these equations are solved in terms of gaseous species concentration (also can be solved in terms of corresponding aqueous species concentrations) rather than total dissolved component concentrations.

65

Appendix 3. Solution of equilibrium chemical system

For simplicity, we only present the case with aqueous reaction and mineral dissolution/precipitation. This formulation is based on principles of the mass balance and mass action (it is easy to include ion exchange and adsorption; details are referred to Xu [1996]). Firstly, N_c mass balance equations, one for each chemical component, can be formulated for each grid block. The total analytical concentration of the j-th component, T_j, is conserved for a closed system, which can be obtained by summing the three terms, concentration of its primary species, concentrations of its associated secondary species, and concentrations of its associated precipitated species

$$T_j = c_j + \sum_{k=1}^{N_X} v_{kj}^x x_k + \sum_{m=1}^{N_P} v_{mj}^p P_m \qquad j = 1...N_C \qquad (A3.1)$$

By substituting (2.35) (where concentration of a second species is expressed in terms of concentration of primary species) into (A3.1), and then by rearranging it, we have

$$F_j^c = c_j + \sum_{k=1}^{N_X} v_{kj}^x (\gamma_k^{-1} K_k^{-1} \prod_{i=1}^{N_C} c_i^{v_{ki}^x} \gamma_i^{v_{ki}^x}) + \sum_{m=1}^{N_P} v_{mj}^p P_m - T_j \qquad j = 1...N_C \quad (A3.2)$$

As mentioned before, no explicit expression relates the concentration of precipitated species at chemical equilibrium, p_m, to the concentration of primary species, c_j. Therefore, N_P mass action additional equations, one for each mineral dissolved/precipitated at equilibrium, must be added to the system of N_C equations (A3.2). Based on (2.53), at equilibrium, we can obtain

$$F_m^p = \frac{\prod_{i=1}^{N_C} c_i^{v_{mi}^p} \gamma_i^{v_{mi}^p}}{K_m} - 1 = \Omega_m - 1 = 0 \qquad m = 1...N_P \qquad (A3.3)$$

N_C equations in (A3.2) and N_p in (A3.3) constitute full set of equations needed for $N_C + N_P$ primary variables, $(c_1, c_2, ..., c_{N_C}, p_1, p_2, ..., p_{N_p})$. This system of nonlinear equations can be solved by Newton-Raphson iteration method. Denoting the set of primary variables collectively as X_i (i=1, 2,..., $N_C + N_P$), we have

$$\sum_{i=1}^{N_C + N_P} \frac{\partial F_j}{\partial x_i} \Delta x_i = -F_j \qquad j = 1...N_C + N_P \qquad (A3.4)$$

where j is row index and i is column index which are opposite to conventional mathematical notation, This is because j in this paper denotes chemical component index and mass balance equations are written in terms of components. In matrix form these equations reduce to

$$\mathbf{J} \cdot \Delta \mathbf{x} = \mathbf{b} \qquad (A3.5)$$

where $\mathbf{J}$ is the Jacobian matrix and $\mathbf{b}$ the vector of residuals. The values of $\Delta \mathbf{x}$ are used to update values of primary variables:

$$x_i^{l+1} = x_i^l + \Delta x_i \qquad (A3.6)$$

where l labels iteration number. The absolute value of the corrections $\Delta \mathbf{x}$ are expected to decrease in successive iterations. The system of equations is considered satisfactorily solved when the values of $\Delta \mathbf{x}$ are below a specified tolerance limit, τ. Due to the different order of magnitude of the unknowns (c_i, p_i) the value of the increment $\Delta \mathbf{x}$ is normalized with respect to $\mathbf{x}$. Therefore, the convergence criteria are:

$$\frac{|\Delta x_i|}{x_i} \leq \tau \qquad i = 1...N_C + N_P \qquad (A3.7)$$

In order to avoid negative values for the concentration of c_i, for all species for which $x_i^{new} < 0$, the largest relative concentration change $\frac{|\Delta x_i|}{x_i}$ is restricted to a specified value $\eta (\eta < 1)$. As a consequence, although the iteration method becomes more robust, the rate of convergence slows down. In cases where a negative value of p_i, is obtained, the i-th mineral is considered exhausted and must be removed from the chemical system, and its corresponding equation disappears. Once the concentrations of primary species are obtained, the concentrations of secondary species can be computed in a straightforward manner. The changes of mineral concentrations, Δp_i, are used to

calculate mass transfer of component j from the aqueous phase to the mineral phase (or mass accumulation), ΔP_j

$$\Delta P_j = \sum_{i=1}^{N_P} v_{ij}^p \, \Delta p_i \qquad j = 1,2,\ldots,N_C \qquad (A3.8)$$

or chemical reaction source/sink terms for transport equations (negative values of mass accumulation rates in the mineral phase), R_j

$$R_j = -\frac{\Delta P_j}{\Delta t} \qquad j = 1,2,\ldots,N_C \qquad (A3.9)$$

Values of ΔP_j or R_j are needed for iteratively solving transport equations (A2.4) as mentioned in Appendix 2.

Acknowledgement

Notation

"Latin"

A	reactive surface area, m^2/kgH_2O.
A	pre-exponential factor of the Arrhenius law.
A_{nm}	area between grid blocks n and m, m^3.
A_m	specific surface area of the mineral, dm^3.
Ar	chemical affinity of a reaction, kcal/mol.
A^*	surface area of the solid per unit mass of solids.
a_x	thermodynamic activity of the species X.
c	concentration of chemical species, mol/l.
C_e	total electron concentration, mol/l.
c_e	free electron concentration, mol/l.
C_H	total proton concentration, mol/l.
c_{H+}	concentration of free proton, mol/l.
C_j	total concentration of the j-th primary species, mol/l.
c_j	concentration of the j-th primary species, mol/l.
c_0	initial concentration.

c^*	source/sink concentration.
C_R	soil grain heat capacity, J/kg ûC.
CEC	cation exchange capacity, meq/100g solid.
D_g^{ij}	binary i-j mixture molecular gas diffusivity, m^2/s.
D_g^{ijR}	reference binary i-j mixture molecular gas diffusivity, m^2/s.
D_g^{j}	molecular diffusivity of mass component j in a multicomponent gas, m^2/s.
$\mathbf{D}$	dispersion tensor.
D_β	molecular diffusion coefficient in phase β.
F^j	total flux of component j; for $j \neq e$: $kg/m^2 s$; for $j = e$: $J/m^2 s$.
$\mathbf{F}_\beta$	total mass flux in the b phase, $kg/m^2 s$.
F_β^j	flux of component j in the b phase; for $j \neq e$: $kg/m^2 s$; for $j = e$: $J/m^2 s$.
F_{nm}	flux from grid block m into n; for mass: $kg/m^2 s$, for heat: $J/m^2 s$.
F	Faraday's constant.
g	magnitude of gravitational acceleration, m/s^3.
$\mathbf{g}$	gravitational acceleration vector, m/s^3.
h	specific enthalpy, J/kg.
h_b	specific enthalpy of phase b, J/kg.
h_g^j	specific enthalpy of mass component j in the gas phase, J/kg.
I	ionic strength.
K	overall porous medium thermal conductivity, W/m K.
K	Thermodynamic equilibrium constant.
$K°$	Thermodynamic equilibrium constant of a surface precursor formation reaction.
K^*	coefficient for cation exchange.
k	porous medium permeability, m^3.
k_d	dissolution rate constant (mol m^{-2} s^{-1}).
k_{rb}	relative permeability of the b phase.
$\mathbf{n}$	unit vector normal to the boundary and pointing outwards.

n	grid block index; also used to denote exponent in the calculation of relative permeabilities and capillary pressures.
n	exponent of the proton activity term (2. 55).
N	inward unit normal vector.
N_C	number of aqueous primary species (component).
N_P	total number of minerals involved in dissol./prec. reactions.
N_w	number of ion exchange reactions.
N_y	number of sorption reactions.
N_R	number of chemical reactions, equal to number of secondary species
N_T	total number of species.
N_w	total number of exchanged species.
N_x	number of aqueous secondary species.
N_y	total number of species sorbed as surface complexes.
m	grid block index; also used to denote exponent in the calculation of relative permeabilities and capillary pressures.
m	exponent of the proton and Al3+ activity term (2. 57.)
M^j	amount of component j per unit porous medium volume (accumulation term);for $j{\neq}e$ (mass components): kg/m^3; for j=e (heat component): J/m^3.
M_n^{κ}	accumulation term for component k in grid block n.
M_{wt}^{aw}	mixture molecular weight of air and water vapor, g/mole.
M_{wt}^{κ}	molecular weight of mass component k, g/mole.
P_{β}	pressure of β, Pa.
q^j	rate of generation of component j per unit volume; for $j{\neq}e$: kg/m^3 s; for j=e: J/m^3 s.
q_b	mass rate of generation of phase b in a source element, kg/s.
P_g^j	pressure fraction of component j in gas phase.
p_i	mass (moles) of the i-th precipitated species per unit fluid volume, mol/l.
P_j	virtual concentration of the j-th primary species in the N_p minerals, kg/m^3 medium.

q^{*j}	rate of generation of component j in a external source element; for mass component: kg/s; for energy: J/s.
S_i	chemical formula of the i-th species.
R	gas constant ($2.99 \ 10^{-03}$ kcal/mol/K).
R	chemical reaction source/sink term, Kg/m^3 s.
r	dissociation reaction rate, mol/l s.
r_m	dissolution/precipitation reaction rate of the m-th mineral, mol/l s.
S_b	saturation of phase b.
S_{br}	residual saturation of phase b.
S_i, S_j	dissolved cation species.
S_i^x	i-th secondary aqueous species.
S_i^p	i-th precipitated species.
S_j	j-th primary species.
T	temperature.
t	time.
u_b	specific internal energy of phase b, J/kg.
u_g^j	specific internal energy of mass component j in the gas phase, J/kg.
V_n	volume of region n of porous medium, m^3.
x	generic notation for primary thermodynamic variable.
X_β^j	mass fraction of mass component j in phase b.
w_i	concentration of the i-th exchanged species, mol/l.
$\overline{w}_i$	activity of the i-th exchanged species.
W_j	virtual concentration of the j-th primary species in the N_w ion exchanged species, kg/m^3 medium.
x_i	concentration of the i-th aqueous secondary species.
$X_{ni} - S_i$	exchange sites which are occupied by the i-th cation.
y_i	concentration of the i-th sorbed species as surface complex, mol/l.

Y_j	virtual concentration of the j-th primary species in the N_y sorbed species, kg/m^3 medium.
z	chemical valence of an element.

"Greek"

β	phase index, b = g: gas phase; l: liguid(aqueous) phase.
β	equivalent fraction of exchanged species.
$\varepsilon_n^{(j),k+1}$	residual of conservation equation for component j in grid block n at time step k+1.
Γ_n	surface area of grid block n, m^3.
Γ	activity coefficient of gas species.
γ	activity coefficient of aqueous species.
ϕ	porosity.
μ_β	β phase viscosity, kg/m s.
ν_{ij}	stoichiometric coefficient of the i-th species in the j-th reaction
ν_{ij}^x	stoichiometric coefficient of the j-th primary species in the dissociation reaction of the i-th aqueous secondary species
ν_{ij}^p	stoichiometric coefficient of the j-th aqueous primary species in the dissolution reaction of the i-th precipitated species
ν_{ij}^y	stoichiometric coefficient of the j-th aqueous primary species in the desorption reaction of the i-th surface complex
ν_i	stoichiometric coefficient of dissolved cations
ν_j	stoichiometric coefficient of interlayer cations
θ	Finite difference time-weighting parameter.
ρ_β	density of the β phase, kg/m^3.
ρ_r	density of rock grain, kg/m^3.
σ_s	surface charge
τ	convergence tolerance, dimensionless.

$\omega^{(j)}$ molecular weight of the j-th chemical species, g/mol.

Ω_m saturation ratio of m-th mineral.

$\nabla .( )$ divergence operator.

$\nabla ( )$ gradient operator.

Δt time step, s.

Δz change in the charge of the surface species.

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